U.S. DEPARTMENT OF COMMERCE
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PB-293 800

EPA/IERL-RTP Procedures for Level 2 Sampling and Analysis of Organic Materials

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Prepared for

Industrial Environmental Research Lab, Research Triangle Park, NC

Feb 79

PB 293800

United States
Environmental Protection
Agency

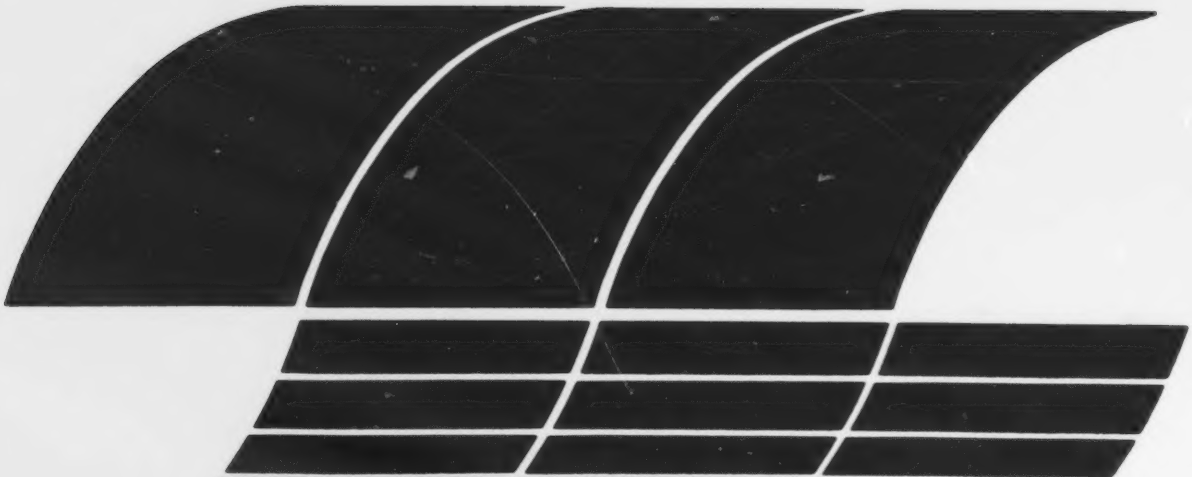
Industrial Environmental Research
Laboratory
Research Triangle Park NC 27711

EPA-600/7-79-033
February 1979

EPA

EPA/IERL-RTP Procedures for Level 2 Sampling and Analysis of Organic Materials

Interagency Energy/Environment R&D Program Report



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TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/7-79-033	2.	3. RECI[illegible] NO. PB293800
4. TITLE AND SUBTITLE EPA/IERL-RTP Procedures for Level 2 Sampling and Analysis of Organic Materials		5. REPORT DATE February 1979 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) J. C. Harris, M. J. Hayes, P. L. Levins, and D. B. Lindsay		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Arthur D. Little, Inc. Acorn Park Cambridge, Massachusetts 02140		10. PROGRAM ELEMENT NO. EHB529 11. CONTRACT/GRANT NO. 68-02-2150, T.D. 21102
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Industrial Environmental Research Laboratory Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED Task Final; 6/77-12/77 14. SPONSORING AGENCY CODE EPA/600/13

15. SUPPLEMENTARY NOTES IERL-RTP project officer is Larry D. Johnson, MD-62, 919/541-2557.

16. ABSTRACT

The manual, giving Level 2 procedures for sampling and chemical analysis of organic materials, represents a step in the development of a general methodology for chemical and biological assessment of environmental effects of industrial effluents. It presents concepts and general guidelines, together with a number of more fully developed, tested, and validated Level 2 procedures. The accumulation of experience in sampling and chemical analysis of environmental pollutants is by no means complete, however. The process is expected to continue for some time, perhaps indefinitely. Users of the manual will therefore find a number of areas in which additional research and testing is needed, and in which present knowledge is insufficient to permit hard and fast procedures to be established.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution	Pollution Control	13B
Sampling	Stationary Sources	14B
Chemical Analysis	Level 2 Procedures	07D
Organic Compounds		07C
Industrial Wastes		
Effluents		

18. DISTRIBUTION STATEMENT Unlimited	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 164
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE MF PCA08/A01

EPA Form 2220-1 (9-73)

EPA-600/7-79-033
February 1979

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Contract No. 68-02-2150
T.D. 21102
Program Element No. EHB529

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Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, DC 20460

GLOSSARY OF TERMS AND ABBREVIATIONS

EPC	Estimated Permissible Concentration
MATE	Minimum Acute Toxicity Effluent
MEG	Multimedia Environmental Goal
TLV	Threshold Limit Value
amu	Atomic Mass Unit
SAM	Source Analysis Model
LRMS	Low Resolution Mass Spectrometry
Gases	Species with boiling point below 100°C
Vapors	Species with boiling point above 100°C
SASS	Source Assessment Sampling System
FAST	Fugitive Air Sampling Train
GC/MS	Gas chromatograph coupled to mass spectrometer
GC/ECD	Gas chromatograph with electron-capture detector
HPLC	High Performance Liquid Chromatography
HRMS	High Resolution Mass Spectrometry
UV	Ultraviolet
RI	Refractive Index (Detector for HPLC)
GPC	Gel-permeation Chromatography
PCB	Polychlorinated Biphenyl
m/e	Ratio of mass to charge

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I. INTRODUCTION

This Level 2 Procedures Manual for sampling and chemical analysis of organic materials represents a step in the development of a general methodology for chemical and biological assessment of environmental effects of industrial effluents. Concepts and general guidelines are presented here, together with a number of more fully developed, tested and validated Level 2 procedures. The accumulation of experience in sampling and chemical analysis of environmental pollutants is by no means complete, however. The process is expected to continue for some time, perhaps indefinitely. Users of this manual will therefore find a number of areas in which additional research and testing is needed, and in which present knowledge is insufficient to permit hard-and-fast procedures to be established.

A. Philosophy of the Phased Approach

The original philosophy used in the development of a phased approach to environmental assessment is briefly reviewed to place the purpose of a Level 2 study in context with the overall program. (1)

The Process Measurement Branch of IERL/RTP has developed a three-tiered or phased approach to performing an environmental source assessment. In this phased approach, three distinctly different sampling and analytical activities are envisioned. (2)

The phased sampling and analytical strategy was developed to focus available resources (both manpower and dollars) on emissions that have a high potential for causing measurable health or ecological effects, and to provide comprehensive chemical and biological information on all sources of industrial emissions.

The phased approach requires three separate levels of sampling and analytical effort. The first, Level 1, is designed to provide enough information about the composition of effluent and process streams to permit them to be ranked in order of priority for probable environmental hazard. The Level 1 assessment is intended to: 1) provide preliminary environmental assessment data, 2) identify principal problem areas, and 3) formulate the data needed for prioritization of energy and industrial processes, streams within a process, components within a stream, and classes of materials, for further consideration in the overall assessment. The second phase of sampling and analysis effort, Level 2, is designed to provide additional information that will confirm and expand the information gathered in Level 1. This information will be used to define control technology needs and may, in some cases, give the probable or exact cause of a given problem. The third phase, Level 3, makes use of sampling and analysis methods whose precision and accuracy are sufficient to permit quantitative monitoring of specific pollutants identified in Level 2. Concentrations of critical components in a stream can thus be determined as a function of time and process variation with accuracy and precision necessary for effective control device development.

The phased approach offers potential benefits in terms of the quality of information that is obtained for a given level of effort and in terms of the costs per unit of information. This approach has been investigated and compared to the more traditional approaches and has been found to offer the possibility of substantial savings in both time and funds required for assessment.

The three sampling and analysis levels are closely linked in the overall environmental assessment effort. Level 1 identifies the questions that must be answered by Level 2, and Level 3 monitors the problems identified in Level 2 to provide information for control device design and development.

B. Purpose of a Level 2 Study

The objective of a Level 2 Study will be to obtain more detailed and accurate data about the composition of a particular process stream than is available in the context of a Level 1 Study. The improved accuracy could either be primarily quantitative in terms of establishing a truly representative emission rate, or be primarily qualitative in terms of determining specific chemical composition, or both. It is expected that most Level 2 sampling and analysis studies for organic compounds will have as an objective the identification of the specific chemical species present and detectable in process streams.

Most Level 2 studies will be probably done as a result of interpretation of data obtained from previous Level 1 studies. Level 2 inquiries are expected to be directed primarily at the identification, quantification and confirmation of specific compounds whose presence could be inferred on the basis of the categorical analysis of Level 1. For these cases, a restricted set of specified procedures may be selected. Level 2 studies may also occasionally be initiated either on the basis of results of the bio-tests alone or on other criteria than the Level 1 chemical analysis. Thus, the questions to be answered by Level 2 procedures may range from highly specific, (i.e., what is the amount and composition of polynuclear aromatics in the stream?) to quite general, (i.e., what caused the positive bio-test results?). In this latter example where Level 1 chemical analysis was apparently not sufficiently sensitive to reveal the existence of a hazardous composition, a comprehensive analytical effort similar to but more exhaustive than that required for Level 1 would have to be conducted. This type of analysis would be characterized as Level 2.

C. Purpose and Scope of This Document

The objective of this document is to present concepts and quidelines to be used in consideration of Level 2 sampling and analysis for organic compounds. This report focuses on concepts and general guidelines, with recommendations and suggestions for specific procedures. Because of the limitation of present experience in conducting Level 2 investigations, many of the procedures recommended herein have necessarily been based on as-yet-unsubstantiated reports of work reported in the literature which seemed in the judgment of the authors to be reliable and applicable to present needs. In some cases, specific tests were performed in our laboratories to establish the adequacy of important procedures. In other cases, advice was offered from other workers in the field of environmental assessment. A directed effort was made to obtain such advice from other contractor laboratories working on related projects for EPA/IERL, and their reactions to the Interim version of this manual were specifically sought and obtained. While the present Manual represents what we believe to be the "state of the art" in its field, the user should be aware that new information is being developed constantly and that further refinements of the recommended methods are to be anticipated.

The Level 2 Organic Procedures Manual is intended for use by experienced research chemists who are presumed to be thoroughly familiar with environmental sampling and analysis, with Level 1 procedures and with the objectives of the phased approach. The manual will not attempt to teach the detail which is more adequately found in other publications, but will rely heavily on reports published previously by IERL-RTP and its contractors (1-8). A reader who is not familiar with these documents should consult them before attempting to use the procedures described in the Level 2 organic sampling and analysis manual.

In addition, various standard methods such as published by ASTM, EPA (Federal Register), NIOSH and the Intersociety Committee are relied upon where appropriate.

The Multimedia Environmental Goals (MEG) study sponsored by IERL-RTP has resulted in the generation of a list of categories of organic and inorganic compounds (the MEG lists) and associated concentration levels representing their toxicity in various media. (8) Examination of these categories shows that they include almost all major classes of organic compounds (with the exception of a very few such as pesticides), and that the MEG list therefore represents a convenient means of organizing a productive approach to organic analysis and reporting of the results of a Level 2 inquiry. The MEG list of organic compound categories has been used advantageously in this manual to provide a practical basis for interpreting data and for selecting Level 2 procedures. Inasmuch as the present document is by no means to be considered final or definitive in its coverage of Level 2 needs, however, the use of the MEG categories should be understood in the context of a reasonable approximation which can be helpful in developing a sound approach to a comprehensive environmental assessment process. It is emphasized that reference to the MEG list in this report is focused on the categories and not on the individual compounds. The MEG categories encompass most groups for which analysis will be needed while the compound list is quite restricted.

II. LEVEL 1 TO LEVEL 2 TRANSITION

The current Level 1 analysis for organic species is expected to result in the description of a number of compound categories and their observed concentrations. Comparison of the measured concentration of each category with an appropriate decision criterion will then establish a basis for proceeding with and/or directing more detailed Level 2 studies. The appropriate decision criteria must be chosen with the concurrence of the Project Officer, bearing in mind the specific objectives of the study for which the Level 1 analysis was conducted. Decision criteria currently under evaluation are the Level 1 0.5 mg/m^3 value for gas emissions, MATE and EPC values from the MEG study, TLV's, S values, and others.

For purposes of illustration, the decision process can be conveniently described using the results of a Level 1 analysis of a stack sample collected with a SASS train, and applying two different sets of decision criteria. Table 1 lists the compound categories found in the sample and their calculated source concentrations.

Each of these concentrations can be compared with a consistent set of decision criteria. In this example, the concentration for each category is compared against the general 0.5 mg/m^3 gaseous emission Level 1 criterion and against the MATE values.

Column 3 shows that four compound categories exceeded the 0.5 mg/m^3 concentration and further studies are indicated for fused aromatics above and below MW 216, heterocyclic nitrogen compounds and carboxylic acids. Column 4 lists the most stringent or "worst case" MATE values for compounds in each of the observed categories. Column 5 gives the results of comparing the observed concentrations with these MATE values. The decision process becomes more complicated when using criteria such as the MATE values because the toxicity data on which they are based are

TABLE 1

Comparison of Level 1 Data with Decision Criteria

Compound Categories	Observed Source Concentration (mg/m^3)	Exceeds Level 1 0.5 mg/m^3	Worst Case MATE (mg/m^3)	Exceeds MATE Value
Aliphatic HC's	0.06	no	200	no
Aromatics - Benzenes	0.06	no	1	no
Fused Aromatics <216	5.	yes	30	no
Fused Aromatics >216	5.	yes	2×10^{-5}	yes
Heterocyclic S	0.2	no	1	no
Heterocyclic N	2.	yes	0.2	yes
Heterocyclic O	0.2	no	590	no
Carboxylic Acids	2.	yes	1	yes
Phenols	0.1	no	2	no
Esters	0.08	no	5	no

III. LEVEL 2 SAMPLING AND ANALYSIS: RECOMMENDED PROCEDURES

A. Sample Types and Sampling Methods

The basic process sample types to be dealt with at each of the levels of sampling and analysis are: any gases which may contain suspended liquid and/or solid particles, liquids and slurries, and solids. Level 2 analyses may be conducted either on samples freshly collected for that purpose or on samples retained from the Level 1 sampling effort. The choice between collecting a new sample or analyzing a retained sample or fraction for the Level 2 data will be highly specific to the exact question to be answered and to the nature of the chemical species to be determined. For example, the Level 2 requirement could be to confirm the presence of and determine the identity of each of several polychlorinated biphenyls (PCB's) in a source. Since the Level 1 sampling procedures are known to be adequate by Level 2 standards for collection of PCB's and since PCB's do not deteriorate in storage, it would usually be sufficient to analyze a retained Level 1 sample to provide the required data. If the Level 2 question pertained to some reactive species or to other material not collected well by the Level 1 methods, then a new specific sampling and analysis effort may be called for, using alternative procedures.

Most of the organic samples retained from the Level 1 study will be in the form of extracts in methylene chloride solution. The Level 1 gas sample for determination of reactive sulfur species and low-molecular-weight hydrocarbon species will not have been retained, having been used for the on-site GC analysis. Some portions of the original solid and particulate samples may be available, since these tend to be more stable than the other samples and to be available in larger quantities than required in the minimum Level 1 procedure.

The Level 1 samples - mostly extract solutions - are conveniently available for more comprehensive organic analytical characterization using all of the techniques discussed later. However, before proceeding

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to more detailed analysis of these (Level 1) samples to answer the Level 2 question, the appropriateness of the sample for study must be carefully evaluated. Does the sample provide a sufficiently quantitative representation of the source? Was the sampling procedure efficient for the species in question? Will the species to be analyzed be stable enough to warrant more detailed analysis? Would an alternative procedure provide a more interference-free sample for analysis? Each of these questions requires a specific answer in each instance, but the general considerations are common to all further Level 2 studies.

In many instances, the results from the Level 1 sampling and analysis study will have triggered specific Level 2 questions. In order to provide better guidance for the selection of specific Level 2 sampling and analysis procedures, further studies on the retained Level 1 samples may be warranted. These might be needed to confirm tentative identifications or to look for species that might interfere with specific methods. However, one should remember that, at best, Level 1 samples still retain all the inherent limitations designed into the selection of sample size, collection methods and extraction procedures. In Level 1, not all categories or species are collected in an optimum manner, since the procedure is required to make certain compromises in the interest of economy and generality. This statement is not a criticism of the Level 1 procedures but rather a reminder that a single set of procedures which attempts to encompass all possible species cannot be expected to be optimized for each specific species or category.

It will be necessary in many cases to collect additional samples for Level 2 studies. The reasons for this include the arguments above about possible limitations of the samples retained from Level 1 and especially, perhaps, the need for providing a more accurate quantitative representation of the entire composition of an effluent or process stream. A new Level 2 sample might also be designed to meet a requirement for quantitative accuracy for specific compounds such as the polynuclear aromatic hydrocarbons (PAH's), aldehydes, phenols, nitrosamines, etc.

The sampling methods available for various categories of sources and compounds are discussed in the following chapter. Review of the available methods has led to recommendation of the sampling techniques described below for general use in Level 2 studies. The techniques are classified according to the type of stream to be sampled - gaseous, liquid or solid - and the state of the organic material - particulate, vapor or gas. Because of the characteristics of the available sampling devices, it is convenient to use a 100°C boiling point cutoff to define the terms "gas" and "vapor." Throughout this report, species with boiling points below 100°C are referred to as gases, while species with boiling points above 100°C are referred to as vapors.

The sample size recommendations that are presented in this discussion are constrained primarily by the need to acquire a sample that is representative of the source and that is large enough for subsequent manipulations (such as weighing and extraction of particulate). The recommendations in this section refer to the total quantity of organic material, except as noted, and do not reflect the analytical detection limit expected for individual chemical species.

1. Gaseous Stack, Vent and Process Streams

The several methods described below are appropriate for sampling of organic species present as entrained particulate, vapors and gases. The sampling devices may be used independently if only one type of species is sought. Alternatively, they may be combined in an integrated sampling system, of which the SASS train is one example, to collect a broader range of materials.

These methods were chosen to be appropriate for a concentration range of about 0.1 to 50 mg/m^3 for the individual organic species of concern. If concentrations very much higher than this are encountered, the capacity of the sampling device(s) may be exceeded unless especially small samples are taken. If concentrations of the individual species of concern are expected to be lower than 10 $\mu g/m^3$, the techniques recommended for ambient air should be used to replace or supplement those listed here.

a. Particulates

A high efficiency, high purity glass fiber filter (e.g., Reeve Angel 934AH) or quartz fiber filter (e.g., Gelman Micro-Quartz) is recommended. If particle sizing is required to provide Level 2 information about the distribution of organic material, one or more cyclones should be used upstream of the filter. The temperature of the filter/cyclone device should be controlled at 195-205°C (380-400°F) during sampling. The volume of gas sampled must be sufficient to ensure collection of at least 100 mg of total particulate material on a filter and at least 500 mg of total particulate material in each cyclone, if possible.

b. Vapors

Adsorption on XAD-2 resin is recommended for most organic categories. The sorbent trap should be thermostatically controlled at 20 ± 2°C during sampling. The dimensions and resin capacity of the sorbent trap, and the volume of gas to be sampled, should be varied as necessary to ensure efficient collection of the species of interest. A procedure for estimation of sorbent sampler design parameters from Vg^T values of the compounds of concern is described in Chapter IV. Some illustrative data are presented in Table 2.

The sample rate is required to be low enough to correspond to a linear gas velocity through the sorbent bed of ≤ 43 cm/sec. The volume of gas sampled must be sufficient to ensure collection of at least 10 to 100 mg of total organic material on the trap.

Organic compound categories for which adsorption on XAD-2 is the recommended vapor sampling procedure are listed in Table 3. It should be noted that, while virtually all types of organic compounds are represented in this list, a number of these categories include some substances with boiling points below 100°C. The vapor sampling procedure is not expected to be effective for those substances whose relatively

Table 2. Sample Size and Flow Rate Comparison for Several Sorbent Trap Designs

	Dimensions, mm		Resin Charge,	Flow equiv to	Maximum Sample Size, m^3 ** for Efficient Collection of		
Trap	depth	diam.	g of XAD-2	43 cm/sec *	Octane	Benzene	Phenol
SASS	70	90	130	165 Lpm (5.9 cfm)	150	3	240
ADL	70	45	40	40 Lpm (1.5 cfm)	45	0.9	74
Battelle	70	30	19	18 Lpm (0.65 cfm)	22	0.4	35

* Upper limit beyond which collection efficiency drops off.

** Calculated from Vg^T for 50% breakthrough. Specified value includes a safety factor of 2.

Table 3. Compound Categories for which Adsorption on XAD-2 is the Recommended Level 2 Vapor Sampling Method

MEG No.	Category
1	Aliphatic Hydrocarbons
2	Alkyl Halides
3	Ethers
4	Halogenated Ethers
5	Alcohols*
6	Glycols, Epoxides
7	Aldehydes, Ketones
8C,D	Amides, Esters
9	Nitriles
10	Amines
12	Nitrosamines
13B	Sulfides, Disulfides
14	Sulfonic Acids, Sulfoxides
15	Benzenes
16	Halogenated Aromatics
17	Aromatic Nitro Compounds
18	Phenols
19	Halophenols
20	Nitrophenols
21, 22	Polynuclear Aromatic Hydrocarbons
23	Heterocyclic N Compounds
24	Heterocyclic O Compounds
25	Heterocyclic S Compounds

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*See also Table 4.

high volatility places them in the category of gases, and which are best sampled by the procedures described in Section C below.

Alternative vapor sampling procedures are recommended to replace or supplement the sorbent trap for a few organic compound categories. Two of these categories, aliphatic alcohols and aliphatic acids, include some compounds with boiling points above 100°C that are inefficiently sorbed by XAD-2. Note, however, that alcohols boiling above about 160°C and acids boiling above 180°C will be collected efficiently on XAD-2. Table 4 presents the alternative methods recommended for the collection of vapors of the lower molecular weight compounds in those categories. Two categories of compounds that are very reactive, hydrazines and mercaptans, also require special sampling techniques. Table 4 presents the methods recommended for substances in all of these categories.

c. Gases

Use of glass bulbs, fitted with high vacuum TFE stopcocks (e.g., Ace Glass catalog No. 8194), is the recommended sample collection method for gases in all categories except as noted below. It is recommended that the previously evacuated bulbs be interfaced to the stack through a probe, glass fiber filter, and critical flow orifice to provide a degree of time integration. (A 0.2 Lpm orifice with an evacuated 2L bulb will give a 12 min total sample time.)

Alternatives to the gas bulb sampling approach are recommended for both gases and vapors of two categories of reactive substances. For hydrazines, continuous collection into bubblers containing 1N aqueous hydrochloric acid is recommended. For aldehydes, use of bubblers containing 1% sodium bisulfite is recommended. Sampling rate should be 21 - 28 Lpm (0.75 - 1 cfm) through the bubblers. The gas volume sampled should be chosen to yield a final analyte concentration of at least 10 μg/mL in the bubbler. Samples should be analyzed within five days of collection. A third category of reactive compounds, the mercaptans, are so reactive that sample collection by direct adsorption on Chromosorb 104,

Table 4. Recommended Level 2 Gas and Vapor Sampling Methods for Certain MEG Categories

MEG. No.	Category	Method	Comment
5	Alcohols	Bubbler; ethylene glycol*	For species with b.p. in range ∼ 100 to 160°C; XAD-2 sorption O.K. for less volatile.
8A,B	Carboxylic Acids	Bubbler; 0.1 N NAOH*	For species with b.p. in range ∼ 100 to 180°C; XAD-2 sorption O.K. for less volatile.
11	Azo Compounds Hydrazines	Bubbler; 0.1 N HCl*	For all hydrazines.
13A	Mercaptans	Collect on Chromosorb 104 Sorbent trap +	

* Sample rate ∼ 30 Lpm. Select gas volume sampled to give ∼ 10 - 100 mg of total organic material per L of bubbler reagent.

+ Sample rate < 43 cm/sec linear velocity. Sample volume collected on Chromosorb 104 to be < 15 L gas/g of sorbent. (Ref. 7) followed by thermal desorption onto a suitable GC column for prompt on-site analysis is recommended.

2. Ambient Air

The several methods described below are appropriate for sampling of organic species present in ambient air as particulate, vapors and gases. These methods were chosen to be appropriate for a concentration range of about 1 to 100 $\mu g/m^3$ for individual organic species of concern. If concentrations much higher than this are encountered (in a fugitive emission sampling situation, for example) the methods described above for stack, vent and process streams should be used to replace or supplement those listed here. For concentrations much lower than 10 $\mu g/m^3$, it will generally be necessary to design and validate a sampling method that is tailored to the particular sampling application and takes account of the interferences suspected of being present.

a. Particulates

A high volume sampling system incorporating a high purity, high performance glass or quartz fiber filter (e.g., Reeve Angel 934 AH or Gelman Micro-Quartz) is recommended. The 5.2 m^3/min (185 cfm) Fugitive Ambient Sampling Train (FAST) sampling system, which incorporates a single stage (15 μm nominal cut off) cascade impactor and a cyclone (3 μm nominal cut off) upstream of the filter, is appropriate.

A sampling rate of 1.4 m^3/min (50 cfm) for the Hi-Vol, to 5.6 m^3/min (200 cfm) for the FAST system is recommended. Sample volume should be chosen to yield at least 500 mg of total particulate material in an 8 - 24 hour period.

b. Vapors

Adsorption on Tenax-GC resin is recommended for most organic categories. Reasons for the choice of this sorbent for sample collection at the low pollutant concentrations characteristic of ambient air are presented in Chapter IV.A.2 of this report. The sorbent trap should be small enough to allow thermal desorption of the entire sample into a GC/MS system. A cartridge containing 250 mg (9 cm long by 0.5 cm I.D.) to 1 g (9 cm long by 1 cm I.D.) of Tenax - GC is suggested. The size of the trap and the volume of gas to be sampled should be varied as necessary to ensure complete collection for the species of interest. A procedure for estimating sorbent sampler design parameters from Vg^T (elution volume) values for the compounds of concern is described in Chapter IV. The Vg^T calculations predict that up to 50 L of air can be sampled per g of Tenax-GC with essentially complete collection of species boiling above 100°C in all compound categories except alcohols and carboxylic acids.

The volume of gas sampled should be sufficient to allow collection of at least 50 - 5000 ng of each individual species of concern on the trap, if possible. A sampling rate of 0.1 to 1 Lpm is recommended to provide some degree of time integration.

The alternative vapor sampling procedures in Table 4 are recommended to replace or supplement the Tenax-GC sorbent trap for the few organic compound categories that are especially inefficiently sorbed or that are very reactive.

c. Gases

The glass sampling bulb approach described above for stacks, vents and process streams is recommended for ambient air sampling of gases. This recommendation must be regarded as tentative, because its applicability to organic gases at low $\mu g/m^3$ concentration levels has not been demonstrated. However, an alternative method of sample acquisition that seems compatible with Level 2 qualitative and quantitative analysis objectives has not been identified. (See Chapter IV.A.1 of this report for a discussion of the limitations in the use of plastic bags as sample collectors.)

3. Aqueous Effluent and Process Streams

Collection of samples from aqueous streams is relatively straightforward. The methodology used for Level 1 is suitable for use in Level 2 as well, except that compositing to acquire a more representative sample is recommended for Level 2 sampling. Either automatic sampling or compositing of manually collected grab samples is acceptable for most organic species of concern. However, samples to be analyzed for very volatile organics (b.p. < ∿100°C) must be sealed into containers with no headspace at the time of collection; manual collection is recommended for those samples. Sampling proportional to flow is recommended for Level 2. Time-proportional sampling is an acceptable alternative if flow is fairly constant.

A minimum sample volume of 1 L is recommended for subsequent extraction. A sample volume of about 50 mL is recommended for analysis of volatiles.

4. Solids, Sludges and Slurries

Methodology used for Level 1 sampling of solids, sludges and slurries is suitable for use in Level 2 as well, except that compositing to acquire a more representative sample is recommended for Level 2.

Flow proportional compositing of manually collected grab samples is recommended. Time proportional sampling is an acceptable alternative if flow is fairly constant. Time proportional sampling is also acceptable in cases where reliable flow measurements cannot be made.

A 500 g to 1 Kg sample is recommended for subsequent extraction.

B. Sample Recovery and Preparation

1. Preparation of Solvent Extracts

a. Particulate, XAD-2 Resin and Solid Samples

Soxhlet extraction with methylene chloride for 24 hours is recommended for each of these types of sample. Pentane is recommended as an alternative extraction solvent if non-polar organics are the only species of concern in a particular Level 2 study. The solvent selected must be compatible with both the sample and the species to be extracted for analysis. For example, solids wet with water will generally not be effectively extracted with pentane.

The size of the Soxhlet extractor and the volume of solvent to be used should be varied according to the quantity of solid material to be extracted. Micro (thimble size: 10 mm dia x 50 mm) and extra-large (thimble size: 75 mm dia x 250 mm) Soxhlet extractors are commercially available and are recommended for quantities < 1 g and > 50 g, respectively. Borosilicate glass thimbles with fritted glass bottoms are recommended for use in the extractors.

Bulk solids should be crushed to a size that will pass a 60-mesh screen before extraction. (10)

b. Aqueous Samples

Liquid-liquid extraction with methylene chloride is recommended for most compound categories. Acceptable alternative solvents include pentane if non-polar organics are the only species of concern, and 15% methylene chloride/85% hexane for pesticides and PCBs.

The pH of the aqueous phase must be adjusted as necessary prior to extraction to ensure adequate recovery of the compound categories of concern. For extraction of organic acids, the pH of the aqueous phase should be adjusted to < 2 with hydrochloric acid. For extraction of organic bases, pH should be adjusted to > 11 with sodium hydroxide. Neutral organics will be equally efficiently extracted at any pH. Serial extractions and back extractions at several pH's can be used to achieve an acid-base-neutral organic fractionation in some Level 2 studies where all three types of organic material are of interest.

Three successive extractions of each sample at each pH are recommended, using 100 mL of solvent per L of sample for each extraction. This recommended procedure can be expected to provide > 90% extraction efficiency for individual organic species that have solvent/water partition coefficients > 12 (log P = 1.08). Extensive listings of partition coefficients between various solvents and water are available (11,12), and these can be used to verify extraction efficiencies for individual organic species of concern. Some illustrative values of log P for heptane, chloroform and octanol are tabulated in Appendix B.

There are several categories of compounds that are not efficiently extracted from water. These include carboxylic acids, sulfonic acids, and glycols. Direct analysis of the aqueous sample is tentatively recommended for those species. An alternative to liquid-liquid extraction is also recommended for organic gases (b.p. < 100°C) in water. A purge and trap approach is suggested below for those species.

2. Concentration of Extracts

It is recommended that Kuderna-Danish evaporators fitted with standard three section Snyder columns be used to concentrate extracts to a final volume of 5-10 mL. Extracts should not be concentrated further if quantitative recovery of species with boiling points in the 100-200°C range is desired. If species with boiling points above 200°C are the only compounds of concern in a particular Level 2 study, the extracts can be concentrated to a volume of 1 mL or less, if necessary, to enhance analytical sensitivity. A micro Snyder column and Kuderna-Danish graduated receiver are recommended for this further concentration step.

3. Clean-up of Sample Extracts

Clean-up of sample extracts is generally recommended prior to analysis by the directed Level 2 procedures, described in Section C of this chapter. The clean-up procedures are intended to minimize interferences and are especially important when a non-selective detector, such as GC/FID, is to be used. Recent Arthur D. Little, Inc., experience has indicated that sample extract pre-cleaning also substantially increases the reliability of the more selective GC/MS analysis. Selection of a clean-up procedure should be based upon the sample matrix type of analysis to be performed and species to be analyzed.

The seven-fraction, silica gel liquid column chromatographic separation procedure (LC) used for Level 1 organic analysis (3) is also recommended for general use in Level 2. An aliquot of the concentrated extract equivalent to 10-100 mg of total organic material should be taken for the LC separation. It is recommended that the LC fractions be recombined prior to analysis, according to the category(ies) of compounds that are being sought in a particular Level 1 study. Table 5 indicates the LC fractions over which the various compound categories are distributed (3). This information should be used to guide the Level 2 recombination scheme. Note that the most logical combinations are not mutually exclusive. In terms of polarity, these are:

aliphatics	LC 1 (or 1, 2)
aromatics	LC 2, 3, 4
slightly polar organics	LC 3, 4, 5
polar organics	LC 5, 6, 7

When more than one compound category is to be sought, the sample can be split to provide, for example, both an LC 2, 3, 4 and an LC 3, 4, 5 pooled sample. An alternative is to analyze both LC 2, 3, 4 and LC 5, 6, 7 for the slightly polar organics such as the heterocyclic O and S compounds.

Table 5. Distribution of Compound Categories in LC Fractions

Compound Categories	LC Fractions						
	1	2	3	4	5	6	7
Aliphatic Hydrocarbons	X						
Alkyl Halides	X	X					
Ethers and Haloethers			X	X	X		
Alcohols					X	X	X
Glycols					X	X	X
Epoxides			X	X	X		
Aldehydes			X	X	X		
Ketones					X	X	X
Carboxylic Acids					X	X	X
Nitriles			X	X	X		
Amines, Azo Cmpds, Nitrosamines					X	X	X
Mercaptans					X	X	X
Sulfides, Disulfides			X	X	X		
Sulfonic Acids, Sulfoxides					X	X	X
Benzenes		X	X	X			
Halo Aromatics		X	X	X			
Nitro Aromatics		X	X	X			
Phenols, Halophenols, Nitrophenols					X	X	X
Fused Polycyclic Aromatics		X	X	X			
Heterocyclic N Compounds (MEG 23A, B, D)					X	X	X
Hererocyclic N Compounds (MEG 23C)			X	X	X		
Heterocyclic O Compounds			X	X	X		
Heterocyclic S Compounds			X	X	X		

Organic acids and bases behave quite similarly in the polarity-based LC separation scheme recommended above. However, it is necessary to separate acids from bases prior to analysis by several of the methods recommended in Section C. These species are concentrated in LC fractions 5, 6 and 7. The clean-up procedures described below for LC 5, 6, 7, could also be done prior to concentration and LC separation if a particular Level 2 study were directed towards acids or bases, but not both. When organic acids and organic bases are both of concern, it will be necessary to divide the fraction(s) containing the polar organic material and clean-up separate aliquots for the subsequent analysis. Note that the LC 5, 6, 7 solvent includes methanol, so the volume of the organic phase will need to be adjusted by addition of methylene chloride after clean-up with aqueous acid or base.

Extracts for GC analysis of phenols should be freed of organic bases (which are incompatible with the recommended phenol GC column) by shaking with three successive portions of 0.1 N aqueous hydrochloric acid. The volume of acid solution used in each step should be 10-20% of the volume of the extract.

Extracts for GC analysis of amines should be freed of organic acids (which are incompatible with the recommended amine GC column) by shaking with three successive portions of 0.1 N aqueous sodium hydroxide. The volume of caustic solution used in each step should be 10-20% of the volume of the extract. Aqueous samples for direct GC or HPLC analysis of carboxylic acids or phenols also require clean-up to remove basic and neutral organic interferences. The pH of the sample should be adjusted to $\geq$ 12 (indicator paper) and the sample extracted with three successive portions of methylene chloride. The organic phase can be discarded if basic and neutral compounds are not of concern in a particular study. The pH of the aqueous solution can be readjusted with hydrochloric acid if necessary prior to analysis.

4. Recovery by Thermal Desorption of Tenax-GC

It is recommended that organic vapors collected from ambient air onto Tenax-GC resin be recovered by thermal desorption. The sampling device should be inserted in, or connected directly to, the injection port of the gas chromatograph with the column oven at room temperature. Details of the interface will vary depending on the GC instrument used. Carrier gas flow through the trap, in a direction opposite to the sample flow direction (backflush), is then introduced to sweep organic vapors onto the cold GC column while the trap is rapidly heated to 200-250°C. A 4-6 min desorb time at elevated temperature is recommended (13 ,14 ,15).

5. Recovery by Purge-and-Trap Method for Aqueous Samples

It is recommended that organic gases be recovered from aqueous samples by purge-and-trap techniques (16 ,17 ,18). A number of purge-and-trap instruments are commercially available and are appropriate for Level 2 use. The following conditions are recommended:

trap:	150 mm x 2.7 mm I.D. stainless steel packed with 100 mm of Tenax-GC and 50 mm of Silica Gel 15
purge cycle:	12 min at 25°C (ambient); 40 mL/min carrier flow
desorb cycle:	backflush trap onto cold (ambient) GC column for 4 min at 180°C; 20 mL/min carrier flow.

C. Recommended Level 2 Analysis Methods by Compound Category

It is expected that most Level 2 organic analyses will be directed towards one or more specific classes of chemical compounds that were indicated by Level 1 analysis to exceed their respective decision-level concentration(s). The Multimedia Environmental Goals (MEG) list (9) generated in an IERL-RTP-sponsored study provides a classification of organic species into 25 categories which represent a convenient means of organizing approaches to Level 2 analysis. This organizational approach does not, of course, mean that only the particular chemical compounds on the MEG list are to be sought for in Level 2 analyses.

Furthermore, it is recognized that there are a few kinds of organic compounds (e.g., pesticides/insecticides, phosphates, silicones) that do not fit neatly into any of the 25 MEG categories and that must be considered separately.

It is, nevertheless, clear that most Level 2 questions can be formulated in terms of determining the identity and abundance of compounds within particular MEG categories.

The analysis methods from which Level 2 methods have been selected are reviewed in Section V of this report. The specific procedures that are recommended for directed Level 2 analysis of organic species in predetermined categories are presented on the following pages. These methods are described in somewhat more detail than was given in the Interim Manual published earlier (19). It is hoped that the level of detail in the present manual will provide valuable guidance to the analyst in selecting analysis conditions that are appropriate for Level 2 study objectives.

Conformance to the recommended methods, to the maximum extent possible, will maximize consistency and comparability among various Level 2 studies. However, each Level 2 study is likely to be unique, and it is necessary to allow for flexibility. Constraints imposed by a particular sample matrix, such as the nature and concentration of potential interferences, may require variation in method details--column liquid phase loading, GC temperatutre program, etc.--at the discretion of the analyst. Also left to the discretion of the analyst is the selection of appropriate internal or external standards, calibration procedures, and quantitative method evaluation procedures (such as recoveries from spiked samples). It is recognized that such analytical quality control procedures, which are critically important in a Level 2 study, will also be uniquely constrained by the particular circumstances of each study. These questions must, therefore, be addressed in the program plan developed for a given Level 2 Environmental Assessment.

Detection limits stated in these methods refer to the quantity of each individual component that the analyst can be expected to reliably quantify in a complex environmental sample. It is recognized that these are somewhat conservative values when compared to the ultimate state-of-the-art of detectability (by GC/MS, for example) in a fairly clean sample matrix.

In general, qualitative identification of specific substances is achieved in the recommended methods by the use of mass spectrometry, coupled wherever possible to gas chromatography (GC/MS). Accurate compound identification is an important objective of Level 2 analysis, and in those instances where GC/MS is either not feasible or not recommended for other reasons, some other technique (IR, LC, LRMS, chemical adduct formation, etc.) should be used for qualitative confirmation.

ALIPHATIC HYDROCARBONS

(MEG CATEGORY 1)

Recommended Method: GC/FID

A. Species with b.p. up to 50°C

Column: Durapak n-Octane/Porasil C, 100/120 mesh,
2mm x 2m stainless steel or glass

Conditions: Flow rate: 25 mL/min
program : 25°C isothermal (Reference A)

(Note: Reference B suggests a complementary column
if necessary.)

B. Species with b.p. in the range 0 - 200°C

Column: 3% SP 2100 on 100/120 Supelcoport
2mm x 3m glass or stainless steel

Conditions: Flow rate: 20 mL/min
Program: 50°C (Reference C)
↓ 6°C/min
200°C

C. Species with b.p. greater than 200°C

Column: 3% Dexsil 400 on 100/120 Supelcoport
2mm x 3m glass or stainless steel

Conditions: Flow rate: 20mL/min
Program: 150°C
↓ 8°C/min
400°C

Detection Limit: 5 ng injected

SUGGESTED ALTERNATIVE METHODS

1. For resolution of very complex mixtures the following capillary column can be used: Sp 2100, 50 meters, 50°C ↓ 2°C/min 200°C
Flow rate 20 cm/sec. Helium.
2. GC/MS can be used for confirmation
3. For separation of very high boiling species, 1% Dexsil 400 on 100/120 Supelcoport, 18" long, glass or stainless steel.

4. GC/MS will give detection limits of about 100 - 500 ng injected.

Note: In addition to the general columns above, Reference B also describes a number of columns giving more specific selectivities.

References:

A. Supelco Catalogue No. 12, p. 28, Supelco, Inc., Bellefonte, PA.

B. Saha, N.C., S.K. Jain and R.K. Dua, "A Generalized and Easily Adaptable Gas Chromatographic Method for the analysis of Gaseous Hydrocarbons", J. Chromatograph Science, 16, 323, (1978)

C. "Separation of Hydrocarbons", Bulletin 745B, Supelco, Inc., Bellefonte, PA.

ALKYL HALIDES

(MEG CATEGORY 2)

Recommended Method: GC/MS

A. For b.p. 20 - 200°C

Column: 0.1% SP 1000 on Carbopack C 80/100 mesh
2mm x 2m Glass or stainless steel

Conditions: Flow Rate: 20mL/min (Reference A)
Program: 175°C isothermal

Expected Retention Times (Reference A)

Chloroalkanes	Carbopack C 0.1% SP-1000 175°C
Methylene chloride	0.50
1,1-Dichloroethane	0.65
Chloroform	0.70
1,2-Dichloroethane	0.75
1,1,1-Trichloroethane	1.00
Carbon Tetrachloride	0.95
Trichloroethylene	1.28
1,1,2-Trichloroethane	1.40
Perchloroethylene	2.25
1,1,1,2-Tetrachloroethane	3.1
1,1,2,2,-Tetrachloroethane	3.3

B. For b.p. greater than 150°C

Column: 3% SP 2250 on 100/120 Supelcoport
2mm x 2m glass or stainless steel

Conditions: Flow Rate: 20mL/min
Program: 100°C isothermal

Detection Limit: 50 ng injected

SUGGESTED ALTERNATIVE METHODS:

1. The useful range of the above columns can be extended if required. The SP 1000 column has a temperature limit of 225°C isothermally or 250°C when programmed. The SP 2250 has a limit of 350°C.

2. GC/ECD is an alternative detector for interference free samples.

Reference:

A. "Carbopack, Graphitized Carbon Black", Supelco Bulletin 738 B, Supelco, Inc., Bellefonte, PA.

ETHERS AND HALOETHERS

(MEG CATEGORIES 3 and 4)

Recommended Method: GC/FID

Column: 3% SP 1000 on 100/120 Supelcoport
2mm x 2m glass or stainless steel

Conditions: Flow Rate: 30 ml/min
Injector: 250°C
Program: 60°C (2 min)
↓ 8°C/min
250°C

Detection Limit: 50 ng Haloethers; 500 ng Ethers

	Expected Retention Times (Min) (Reference A)
2-chloroethyl vinyl ether	2.68
Bis (2-chloroethyl) ether	8.35
Bis (2-chloroethoxy) methane	13.02
4-chloro phenyl phenyl ether	19.34
4-bromo phenyl phenyl ether	21.08

SUGGESTED ALTERNATIVE METHODS:

1. Chemical ionization mass spectroscopy can be used for qualitative identifications.
2. Haloethers may be determined by GC/MS with a 50 ng detection limit.
3. For haloethers free from interferences:
   A. The Hall Electroconductivity detector can be used
   Conditions: Furnace temperature 850°C
   Hall Electrolyte flow: 5 mL min, 24 mL/min^{-1}
   Hall electrolyte makeup: 50 mL/min^{-1} H_2.

   B. The electron capture detector can be used.

Reference:

A. Levins, Philip L., and Kathleen E. Thrun, "Analytical Methods Recommendations for Organic Priority Pollutants for the Chemicals and Plastics Industry Category Verification Study", Submitted as part of monthly progress report No. ADL 79347-23, EPA Contract No. 68-02-2150, May, 1978.

ALCOHOLS

(MEG CATEGORY 5)

Recommended Method: GC/FID

A. For b.p. up to 200°C
Column: .1% SP 1000 on Carbopack C
2mm x 2m Glass.
Conditions: Flow rate: 20 mL/min
Program: 100°C
↓ 8°C/min
225°C

Expected Retention Times (Reference A)

Methyl alcohol	.6 min
Ethyl alcohol	.8 min
Isopropyl alcohol	1.2 min
Isobutyl alcohol	2.8 min
n-Butyl alcohol	3.8 min

B. For b.p. greater than 200°C
Column: 3% SP 2100
on 100/120 mesh Supelcoport (Reference B)
2mm x 3m glass
Conditions: Flow Rate: 20 mL/min
Program: 225°C isothermal

Detection Limit: 50 ng injected

SUGGESTED ALTERNATIVE METHODS:

1. Chemical ionization mass spectroscopy detection may be applicable to this category

References:

A. "Solvent Mixtures and Determination of Water in Solvents", Supelco Bulletin 747C, Supelco Inc., Bellefonte, PA.

B. Supelco Catalog No. 12, p. 5, Supelco Inc., Bellefonte, PA.

GLYCOLS, EPOXIDES

(MEG CATEGORY 6)

At this time no satisfactory general method has been found for analysis of this category, although the 3% SP 1000 column may be suitable for some compounds.

ALDEHYDES AND KETONES

(MEG CATEGORY 7)

A. Aldehydes

The recommended method for this category is the 5-Methyl-2 Benzothiazolone Hydrazone (MBTH) method for total aldehydes in air. Sample air is bubbled through an aqueous solution of MBTH, allowed to react for 1 hour after sampling is stopped, an oxidizing agent is added and the absorbance measured at 628 nm. The detection limit is approximately 1 - 10 ppb in air. (Reference A)

B. Ketones

Recommended Method: GC/MS

Column: 3% SP 2250 on 100/120 Supelcoport
2mm x 2m, glass

Conditions: Flow Rate: 20 mL/min
Program 60°C
↓ 6°C/min
200°C

Detection Limit: 50 ng injected

SUGGESTED ALTERNATIVE METHODS:

None recommended.

Reference:

A. Hauser, Thomas, R. and Rodney L. Cummins, "Increasing Sensitivity of 3-methyl-2-Benyothiayolone Hydrazone Test for Analyses of Aliphatic Aldehydes in Air", Analytical Chemistry, 56, 679 (1964)

CARBOXYLIC ACIDS

(MEG CATEGORY 8a-b)

(Note: The methods proposed for all substances in this category must be regarded as tentative, pending demonstration of their effectiveness for environmental assessment.)

A. Formic, acetic acids,
Mono-acids to C5

Recommended Method: GC/MS

Column: Carbopack B/3% Carbowax 20 M/0.5% H_3PO_4,
30" (76cm) x 4mm I.D. glass

Conditions: Flow Rate: 60 mL/min
Program: 160°C isothermal

Detection Limit: 50 ng injected

	Expected Retention Times (Reference A)
formic	<1 min.
acetic	1 min.
propionic	1.6 min.
isobutyric	3.6 min.
n-butyric	5 min.
n-valeric	15 min.

B. Dicarboxylic acids, aromatic acids, aliphatic acids >C5, and acids with additional functional groups

Recommended Method: Reverse Phase HPLC (Reference A)

Column: MicroPak-CH (octadecylsilane), μBondapak/C_{18}

30cm x 4mm I.D., or equivalent

Mobile phase: water, acidified to pH 2.5 with $HClO_4$ and operated at 60°C for MicroPak-CH; Water Methanol mixtures for μBondapak C_{18}; ∿ 2mL/min.

Detector: UV, (variable wavelength) at 210nm for aliphatic acids, and 254nm for others.

Detection Limit: 1 - 100 μg/mL, (50μL injected.)

SUGGESTED ALTERNATIVE METHODS:

1. For samples in which known interferences are absent:
Determination of acids as methyl or methylsilyl esters,

with detection by GC/FID.

2. Ion-exchange liquid chromatography, using either:
   (1) cation-exchange resins (Dowex 50W-X4 or Aminex 50W-4X) with 0.001N or 0.01N HCl eluent, or;
   (2) Strongly basic anion-exchange resins (e.g. Dowex 1-X8), with 0.2M NaOAc and HOAc as eluents. Detection by RI or UV at 210nm or 254nm as appropriate. (Reference B).

References:

A. Supelco Catalog No. 13, p. 3, Supelco, Inc., Bellefonte, PA.

B. Richards, M., "Separation of Mono and Dicarboxylic Acids by Liquid Chromatography", Journal of Chromatography, 115, 259 (1975).

AMIDES

(MEG CATEGORY 8C)

Recommended Method: GC/MS

Column: 3% Dexsil 400 on 100/120 mesh Supelcoport
2mm x 3m glass

Conditions: Flow Rate: 20mL/min
Program: 150°C
↓ 8°C/min
300°C

Detection Limit: 50 ng injected.

ESTERS

(MEG CATEGORY 8D)

Note: (The following tentative method was developed primarily for species such as phthalate esters but is expected to be applicable to a wide range of esters.)

Recommended Method: GC/MS

Column: 3% SP 2250 on 100/120 mesh Supelcoport
2mm x 2m glass

Conditions: Carrier: 20 mL/min
Program: 100°C

$$\Big\downarrow \; 6^\circ C/min$$

280°C

Detection Limit: 50 ng injected

NITRILES

(MEG CATEGORY 9)

Recommended Method: GC/MS

Column: 3% SP 1000 on 100/120 Supelcoport
2mm x 2m glass

Conditions: Flow Rate: 30 mL/min
Program: 100°C

$$\downarrow \ 8°\mathrm{C/min}$$

250°C

Detection Limit: 50 ng injected

SUGGESTED ALTERNATE METHODS:

1. Flame Ionization Detection can be used for interference-free samples.

AMINES

(MEG CATEGORY 10)

Recommended Method: GC/MS

Column: 4% Carbowax 20 M on Carbopack B + .8% KOH
2mm x 2m Glass

Conditions: Flow Rate: 20 mL/min N_2

Program: 100°C
↓ 8°C/min
200°C

Expected Retention Times (Reference A)

Amine	125°C	175°C
Methyl	0.65 min	- min
Dimethyl	0.95	-
Ethyl	1.0	-
Trimethyl	1.15	-
Isopropyl	1.65	0.75
n-Propyl	2.05	0.85
t-Butyl	2.75	1.
Diethyl	3.55	1.2
sec-Butyl	3.9	1.3
Isobutyl	4.2	1.35
n-Butyl	5.45	1.6
Isoamyl	12.3	3.
n-Amyl	-	3.45
Diisopropyl	11.	2.70
Triethyl	-	2.8
Dipropyl	-	4.7
Ethylenediamine	4.5	1.5
Piperidine	8.3	2.25
Pyridine	10.2	2.55
Morpholine	11.3	2.75
1,3-Propanediamine	-	2.95
Piperazine	16.4	3.7
Cyclohexyl	25.	5.1
1-4- Butanediamine	-	-

Detection Limit: 50 ng injected

SUGGESTED ALTERNATIVE METHODS:

1. For High boiling amines:

   10% Carbowax 20 M - 2% KOH on 80/100 Chromosorb W AW, 2mm x 2m glass, column temperature 200°C, Flow Rate: 20 mL/min^{-1}, RT for nicotine is approximately 3.2 min. (Reference A)

2. For Non-volatile amines:

   HPLC can be used. Young and McNair (Reference B) have separated a wide variety of high-MW amines using several different silica gel columns.

3. An alternate detector for preliminary GC evaluation is the FID.

References.

A. "Amine Analysis", Supelco Bulletin 737B Supelco Inc., Bellefonte, PA.

B. Young, Philip R., and Harold M. McNair, "High Pressure Liquid Chromatography of Aromatic Amines", Journal of Chromatography, 119 (1978) 569-579.

AZO COMPOUNDS AND HYDRAZINES

(MEG CATEGORY 11)

The recommended method for this category is an approved NIOSH method for phenylhydrazine and 1,1 -dimethylhydrazine and is expected to be general for all hydrazines. (Reference A)

The collected sample is reacted with phosphomolybdic acid to form a complex with a strong adsorption maximum at 750 nm. The detection limit is approximately 5 mg/m^3 in air.

Reference:

A. NIOSH Manual of Analytical Methods, Second Edition, Method No. S160.

Nitrosamines

(MEG CATEGORY 12)

Recommended Method: GC/MS

Column: 3% SP 2100 on 100/120 Supelcoport
2mm x 3m Glass

Conditions: Flow rate: 20 mL/min
Program: 90° isothermal

Expected Retention Times (Reference A)

N-Nitrosodimethyl amine	1.3 min
N-Nitrosodipropyl amine	11 min

Detection Limit: 50 ng injected.

SUGGESTED ALTERNATIVE METHODS:

1. An alternative column is a 4% Carbowax 20 M + 0.8% KOH 2mm x 2m glass (see amine analysis)
2. Alternate detectors are
   a. Alkali flame ionization detector
   H_2 - 6 mL/min^{-1}

   b. Hall (electroconductivity)
   c. ECD
3. For non-volatile species the following HPLC columns can be used:
   a. µ Porasil 30cm x 4mm
   5% acetone/95% isoactane 2 mL/min
   b. µ Bondapack-C/V 30cm x 4mm I.D.
   1.5% acetonitrite, 98.5% isooctane
   1.5 mL/min, detection is either by UV at 254 nm or with a thermal energy analyzer.

Reference:

A. Levins, Philip L., and Kathleen E. Thrun, "Analytical Methods Recommendations for Organic Priority Pollutants for the Chemical and Plastics Industry Category Verification Study", Submitted as part of monthly progress report No. ADL 79347-25, EPA Contract No. 68-02-2150, May, 1978.

MERCAPTANS, SULFIDES, DISULFIDES

(MEG CATEGORY 13)

Recommended Method: GC/MS

A. For b.p. 6-60°C

Due to the difficulty of storing species such as Methyl Mercaptan, these should be analyzed by on-site G.C. using the column specified by the Level 1 procedure.

B. For b.p. greater than 60°

Column: 3% SP 1000 on 100/120 Supelcoport 2mm x 2m glass

Conditions: Flow Rate: 20 mL/min
Program: 100°C
↓ 6°C/min
200°C

Detection Limit: 50 ng injected

SUGGESTED ALTERNATIVE METHODS

1. The following column has been used to separate low molecular weight compounds in this category; Chromasil 330, 2mm x 2 m Teflon, Flow Rate: 20 mL/min, Temperature 65°C (retention of N-butyl mercaptan = 8 min, methyl disulfide 9 min.) (Reference A)

2. Flame photometric (Reference B) or flame ionization detection can be used for interference-free samples.

References:

A. "Analysis of Sulfur Gases", Supelco Bulletin 722F, Supelco Inc., Bellefonte, PA.

B. Stevens, R.K., and A.E. O'Keefe, Analytical Chemistry, 42, 142-A (1970).

SULFONIC ACIDS, SULFOXIDES

(MEG CATEGORY 14 a-b)

Note: (The methods proposed for all substances in this category must be regarded as tentative, pending demonstration of their effectiveness for environmental assessment.)

A. Sulfonic acids

Recommended Method: reverse-phase ion-pair liquid partition chromatography (Reference A)

Column: LiChrosorb SI 60 silanized or Bondapak C_{18}/Porasil B coated with 10% tri-n-octylamine; 185 - 300mm x 3mm I.D.

Mobile Phase: Tetrabutylammonium in aqueous phosphate buffer, pH 7.4; or aqueous perchloric acid in pH ∿2-6. Maintained at 25° Eluted at 0.7 - 2.5 mm/sec.

Detector: UV at 254 nm

Detection Limit: 10 - 50 ng injected

B. Sulfoxides

Recommended Method: GC/MS

Column: 3% SP 1000 on 100/120 Supelcoport
2m x 2mm glass

Conditions: Carrier: 30mL/min
Program: Isothermal 165°

Detection Limit: ∿ 50 ng injected (each component)

SUGGESTED ALTERNATIVE METHODS:

None Recommended.

Reference:

A. Kraak, J.C. and Huber, J.F.K. J. Chromatography 102 (1974) 333-351; Wahlund, K.G. ibid. 115 (1975) 411-422.

BENZENE AND SUBSTITUTED BENZENE HYDROCARBONS

(MEG CATEGORY 15)

Recommended Method: GC/MS

A. For boiling point range: 80 - 200°C

Column: .1% SP 1000 on 80/100 mesh Carbopack C
2mm x 2m glass or stainless steel (Reference A)

Conditions: Flow Rate: 20 mL/min
Program: isothermal at 225°C

Detection Limit:

Expected Retention Times (Reference A)

	200°C	225°C
n-Hexane	1.15 Min	0.8 Min
n-Heptane	2.30	1.45
n-Octane	5.30	3.0
n-Nonane	12.8	6.7
Benzene	0.95	0.70
Toluene	2.28	1.47
Ethylbenzene	3.90	2.38
Isopropylbenzene	5.36	3.15
m & p-Xylene	6.60	3.60
o-Xylene	7.30	4.00
n-Propylbenzene	8.56	4.70
1,3,5-Trimethylbenzene	-	9.95
1,2,4 Trimethylbenzene	-	12.1
1,2,3-Trimethylbenzene	-	13.3
tert-Butylbenzene	-	4.55
sec-Butylbenzene	-	5.25
Isobutylbenzene	-	7.45
n-Butylbenzene	-	10.05

B. For boiling point range > 110°C

Column: 3% SP 2250 or equivalent on 100/120 mesh supelcoport
2mm x 2m glass or stainless steel. (Reference A)

Conditions: Carrier 20 mL/min
Program: 70°C

$$\downarrow \ 10°C/min$$

300°C

Sample Chromatogram (Reference A)

Expected Retention Times

1,3,5-trimethylbenzene	9.2 min.
1,2,4-trimethylbenzene	10.9 min.
1,2,3-trimethylbenzene	13.9 min.
1,2,4,5-tetramethylbenzene	22.0 min.
1,2,3,5-tetramethylbenzene	23.5 min.
1,2,3,5-tetramethylbenzene	29.1 min.

SUGGESTED ALTERNATIVE METHODS:

1. GC/FID is an alternative for samples free of interferences.

2. An alternate column for low boiling aromatics is a .2% Carbowax 1500/ Carbopack C 2mm x 2m glass or stainless steel.

   Conditions: Flow Rate: 20 ml/min

   Program: 60°C (3 min)

   ↓ 8°C/min

   160°C

   Retention of ethylbenzene is 20 min. (References B,C)

References.

A. "Separation of Hydrocarbons", Bulletin 743 B, Supelco Inc., Bellefonte, PA.

B. "Carbopack", Bulletin 738 B, Supelco Inc., Bellefonte, PA.

C. "Water Pollution Analysis and Standards" Bulletin 775, Supelco, Inc. Bellefonte, PA.

HALOGENATED AROMATIC COMPOUNDS

(MEG CATEGORY 16)

Recommended Method: GC/MS

Column: 3% SP 2250 on 100/120 Supelcoport
2mm x 2m Stainless steel or glass

Conditions: Flow Rate: 30 mL/min
Program: 75°C
↓ 8°C/min
260°C (for 15 min)

Detection Limit: 10 ng injected

Retention Times for 1% SP 2250 (Reference A)

1,3 Dichlorobenzene	6.8 min
1,2,4 Trichlorobenzene	10.6 min
4,4' DDD	25.8 min
Hexachlorobenzene	19.4 min

SUGGESTED ALTERNATIVE METHODS:

1. GC/ECD is an alternative detection system.

References.

A. "Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants," U.S. EPA, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, March 1977 (Revised April 1977).

AROMATIC NITRO COMPOUNDS

(MEG CATEGORY 17)

Recommended Method: GC/MS

Column: 3% SP 2250 on 100/120 Supelcoport
2mm x 2m glass or stainless steel (Reference A)

Conditions: Flow Rate: 30 mL/min
Program: 100°C
↓ 10°C/min
350°C

Detection Limit: 10 ng injected

SUGGESTED ALTERNATIVE METHODS:

1. GC/FID or ECD is an alternative detection system for preliminary evaluation, for interference free samples.
2. An alternate column is 1.5% SP 2250 + 1.95% SP 2401 on 100/120 Supelcoport, 2mm x 2m,

   80°C
   ↓ 8°C/min
   300°C (Reference B)

References.

A. Goerlitz, D., F., L.M. Law, "G.C. Method for the Analysis of TNT and RDX Explosives Contaminating Water and Soil Core Material", U.S. Department of the Interior, Geologic Survey, Water Resources division, Report 75-182 (1975).

B. Jones, Peter W., Anthony P. Graffeo, Ralph M. Rigger and Paul E. Strup, "Development of Methods for Analysis Benzidines, PAHs, Nitrobenyenes and Isophorone in Industrial Wastewater", Monthly Progress Report, Battelle, Columbus Labs, Contract No. 68-03-2624, March, 1978.

PHENOLS, NITROPHENOLS, HALOPHENOLS

(MEG CATEGORIES 18, 19, 20)

Recommended Method: GC/MS

Column: 1% SP 1240 DA on 100/200 Mesh
Supelcoport; 2m x 2mm glass

Conditions: Carrier: 30 mL/min
Program: 85°C (4 min)

$$\downarrow \; 10°/\text{min}$$

200°C

Detection Limit: 50 ng injected

Expected Retention Times (Reference A)

	1 m Column	2 m Column
o-chlorophenol	1.7 min	3.9
o-nitrophenol	2.1 min	5.1
phenol	3 min	6.9
2,4-dimethylphenol	4 min	8.8
2,4,6-trichlorophenol	6 min	12
2,4-dinitrophenol	10 min	16
pentachlorophenol	12 min	17

SUGGESTED ALTERNATIVE METHODS:

1. For samples free of interferences:

   GC/FID; same chromatographic conditions as above. Detection Limit: 1-10 ng injected

2. For non-volatile phenols (e.g., hydroxy-BaP) and/or direct analysis of phenols in aqueous samples:

   HPLC, Reverse phase
   Column: μ Bondapak-C_{18}, 4 mm x 300 mm
   Mobile Phase: water: ethanol:: 60:40
   40 mL/hr
   Detector: UV at 254 nm
   Detection Limit: 10-50 ng injected

Reference:

A. Levins, Philip L., and Kathleen E. Thrun, "Analytical Methods Recommendations for Organic Priority Pollutants for the Chemicals and Plastics Industry Category Verification Study", Submitted as part of monthly progress report No. ADL 79347-23, EPA Contract No. 68-02-2150, May, 1978.

POLYNUCLEAR AROMATICS

(MEG CATEGORIES 21, 22)

Recommended Method: GC/MS

Column: 3% Desil 400 on 80/100 mesh Supelcoport
2mm x 3m, glass or stainless steel

Conditions: Flow Rate: 30 mL/min
Program: 100°C (2 min)
↓ 8°C/min
375°C (Reference A,B)

Detection Limit: 10 ng injected

SUGGESTED ALTERNATIVE METHODS:

1. GC/FID is an alternate detection system.
2. For very complex samples requiring greater separating power or for resolution of Benz(a)pyrene and Benz(e)pyrene the following capillary column can be used:

   Column: .25mm x 20m SE-52 glass capillary
   Conditions:
   Program: 150°C
   ↓ 5°C/min
   275°C (Reference C)

3. The following reverse phase HPLC method has been used to analyze 18 PNA's from napthalene to indeno (1,2,3-cd) pyrene with detection limits from 0.01 to 1.0 ppb. Perkin Elmer HC-ODS column, 40% acetonitrile in water, isocratic for 5 min.; then gradient elution to 100% acetonitrile in 25 min. Flow rate: 0.5 ml/min.

References:

A. Lao, R.C., R.S. Thomas, H. Oja, L. Dubois, "Application of a GC/MS/ Data Processing System Combination in the Analysis of the Polycyclic Aromatic Hydrocarbon Content of Airborn Pollutants" Analytical Chemistry, pp. 45, 908, (1973).

B. Cautreels, W., K. Van Cauivenberlke, "Fast Quantitative Analysis of Organic Compounds in Airborn Particulate Matter by Gas Chromatography with Selective MS Detection", J. Chromatography, pp. 151, 253 (1977).

C. Strup, Paul E., Jo Ann E. Wilkinson, and Peter W. Jones, "The Trace Analysis of Polycyclic Aromatic Hydrocarbons in Aqueuous Systems using XAD-2 Resin and Capillary Column GC/MS Analysis," Battelle Columbus Labs, Columbus, Ohio.

D. Personal Communication: Battelle Columbus Laboratories to Arthur D. Little, Inc., RFP No. RJ-4253, December 7, 1978.

HETEROCYCLIC NITROGEN COMPOUNDS

(MEG CATEGORY 23)

Recommended Method: GC/MS

Column: 3% Desil 400 on 100/120 mesh Supelcoport
2mm x 3m glass or stainless steel

Conditions: Flow Rate: 60 mL/min
Program: 160°C
↓ 8°C/min
300°C (Reference A)

Detection Limit: 10 ng injected

SUGGESTED ALTERNATIVE METHODS:

1. GC/AFID or GC/FID for samples free from interferences.

2. For complex samples requiring greater separating power:

   Column: SE-52 glass capillary - average phase thickness: .29μ
   25mm x 20 M

   Conditions:
   Program: 100°C
   ↓ 4°C/min
   280°C (Reference B)

Heterocyclic Nitrogen Compounds (MEG Category 23) (Continued)

References:

A. Dong, Michael W., David C. Locke and Dietrich Hoffman, "Characterization of Aza Arenes in Basic Organic Portion of Suspended Particulate Matter" Environmental Science and Technology, 11, 612 (1977)

B. Lee, M.L., K.D. Bartle and M.V. Novotny, "Profiles of the PN-1 Fraction from Engine Oils Obtained by Capillary Column G.C. and Nitrogen Selective Detection", Analytical Chemistry, 47, 540 (1975)

HETEROCYCLIC OXYGEN COMPOUNDS

(MEG CATEGORY 24)

Recommended Method: GC/MS

Column: 3% SP 1000 on 100/120 Supelcoport
2mm x 2m

Conditions: Flow Rate: 30 mL/min
Program: 100°C
↓ 10°C/min
250°C

Detection Limit: 10 ng injected

SUGGESTED ALTERNATIVE METHODS:

1. GC/FID for preliminary evaluation or samples free of interferences.
2. Additional Resolution may be obtained using the alternate column described for category 23.

HETEROCYCLIC SULFUR COMPOUNDS

(MEG CATEGORY 25)

Recommended Method: GC/MS

A. For b.p. range 80 - 200°C (Purge-and-trap or organic extract)

Column: 0.1% SP 1000 on Carbopack C 80/100 mesh
2mm x 2m Glass or stainless steel.

Conditions: Flow Rate: 30 mL/min
Program: isothermal at 225°C

B. For b.p. range > 110°C

Column: 3% SP 2250 on 100/120 mesh supelcoport
2mm x 2m Glass or Stainless Steel.

Conditions: Carrier:
Program: 70°C

$$\Big\downarrow \; 10^\circ\mathrm{C/min}$$

350°C

Detection Limit: 10 ng injected

SUGGESTED ALTERNATIVE METHODS:

1. GC/Flame Photometric detection or GC/FID for preliminary evaluation or for samples free of interferences.

2. The SE-52 capillary column described for category 23 can be used if resolution is a problem. (Reference A)

Reference.

A. Lee, M.L., and Ronald Hites, "Characterization of Sulfur Containing Polycyclic Aromatic Compounds in Carbon Blacks." Analytical Chemistry, Vol. 48, 1890 (1976).

PESTICIDES AND PCB's

Recommended Method: GC/MS

The following method is used by U.S. EPA (Reference A).

Column: 1.5% SP 2250 and 1.95% SP 2401 on
100/120 Supelcoport 4 mm X 2m glass.

Conditions: Flow Rate: 70 mL/min
Program : 200°C isothermal

Expected Retention Times

Group 1 Pesticides	(Aldrin=1)	RT'	Group 2 Pesticides	RRT	RT
α-BHC	.56	1.35	α-BHC	.71	1.70
β-BHC	.79	1.90	Heptachlor	.83	2.00
δ-BHC	.90	2.15	Aldrin	1.00	2.40
Heptachlor-epoxide	1.46	3.50	Endosulfan I	1.87	4.50
DDE	2.14	5.13	Dieldrin	2.27	5.45
DDP	3.26	7.83	Endrin	2.73	6.55
DDT	3.92	9.40	Endosulfan II	3.33	8.00

Detection Limit: 50 ng injected

SUGGESTED ALTERNATIVE METHODS:

1. The SP 2250 column described for Halogenated Aromatics (MEG Category 16) can also be used for this group.
2. ECD is an alternative detector.

Reference:

A. Federal Register Vol. 38, Number 125, part II, pp. 17318 - 17323, Friday, June 29, 1973.

D. RECOMMENDATIONS FOR ANALYSIS OF UNKNOWN SAMPLES

In some cases, a need for Level 2 studies may be indicated by criteria other than the results of Level 1 chemical analysis. Such criteria might include, for example, a set of positive biotest results, rather than chemical composition data. The biotest results would not target specific chemical categories for study in Level 2. In these cases a comprehensive set of Level 2 studies will be required using procedures with lower detection limits than Level 1. It may also be necessary to analyze for species which may originally have gone undetected because of the procedural constraints imposed by the Level 1 economic considerations. A general approach for these unknown samples is discussed in this section.

Samples to be analyzed at Level 2 for which Level 1 failed to provide a more directed analysis will generally have to be analyzed by methods that have greater detection sensitivity for specific compounds (i.e., lower detection limits) than those used in Level 1, and that deal better with those areas for which Level 1 procedures are least well suited, for instance gases and high molecular weight species. It will be important to provide assurance that no significant portion of the collected sample has failed to be accounted for in the analysis, and that qualitative detail is adequate to meet the requirements of the inquiry.

It is difficult to devise a specific scheme that will be appropriate for all process streams to be analyzed in this manner. This section seeks to present some general guidance and suggestions of procedures to be used and the sequence in which they should be used.

A general scheme that should be useful in planning a Level 2 analysis is given in Figures 1.a. and 1.b. Three general types of samples are considered; (1) those that are essentially gaseous, but may contain suspended solid or liquid aerosols; (2) those that are

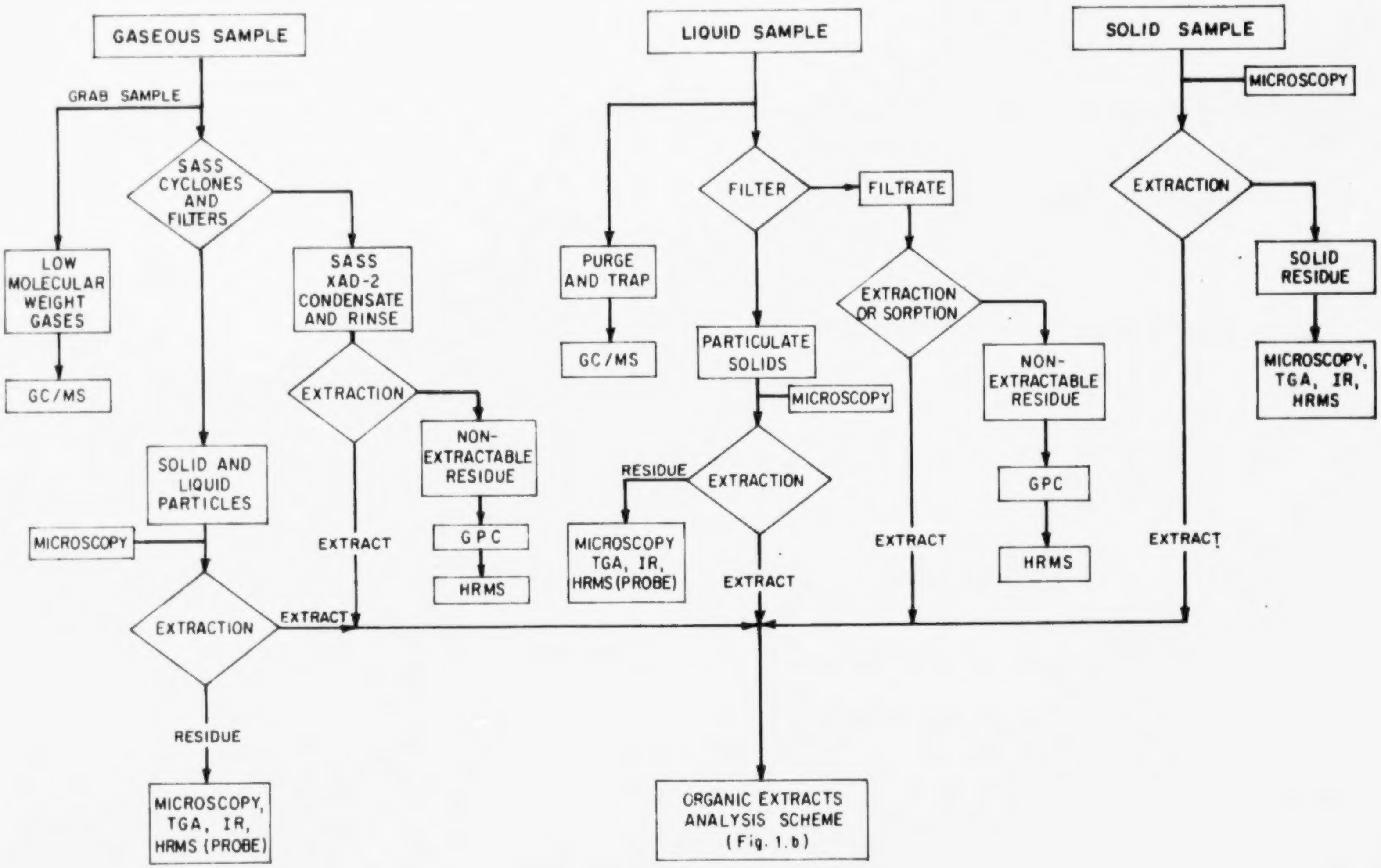


FIGURE 1.a. LEVEL 2 ORGANIC ANALYSIS SCHEME.

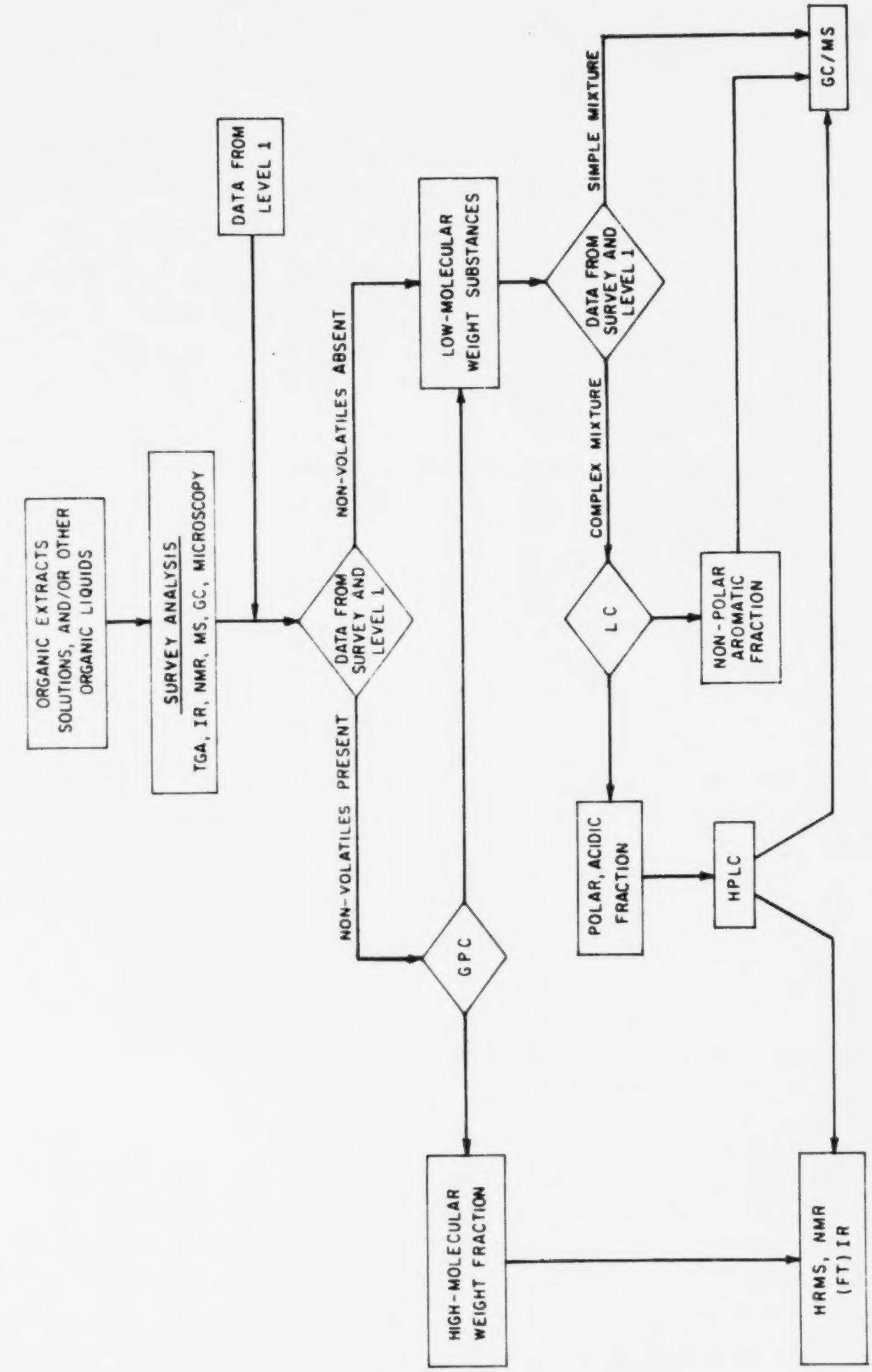

ORGANIC EXTRACTS SOLUTIONS, AND/OR OTHER ORGANIC LIQUIDS
SURVEY ANALYSIS
TGA, IR, NMR, MS, GC, MICROSCOPY
DATA FROM LEVEL 1
DATA FROM SURVEY AND LEVEL 1
NON-VOLATILES PRESENT
NON-VOLATILES ABSENT
GPC
LOW-MOLECULAR WEIGHT SUBSTANCES
HIGH-MOLECULAR WEIGHT FRACTION
DATA FROM SURVEY AND LEVEL 1
COMPLEX MIXTURE
SIMPLE MIXTURE
LC
POLAR, ACIDIC FRACTION
NON-POLAR AROMATIC FRACTION
HPLC
GC/MS
HRMS, NMR (FT) IR

FIGURE 1.b. ORGANIC EXTRACTS ANALYSIS SCHEME.

essentially liquid -- often aqueous -- but that may contain dissolved gases, liquids and solids as well as suspended solid particles; and (3) those that are principally solid, and which may contain some entrained liquids.

Samples from the gas phase (e.g., from stacks, ducts and ambient air) are expected to be collected principally by direct "grab" sampling, using glass bulbs, and by the SASS train or similar devices, such as, for example, the modified Method 5 train. The "grab" samples may be analyzed directly, using appropriate GC and/or GC/MS techniques, or they may be pre-concentrated by adsorption at low temperature on resins such as Tenax-GC, from which they can be thermally desorbed for GC and/or GC/MS analysis.

The samples collected by an atmospheric sampling train such as SASS pass through the cyclones and filters that are included in those systems to remove and collect suspended solids, and are then led through a sorbent resin trap (XAD-2) to collect vapors of organic compounds. Some organic vapors condense on the walls of the SASS train components and some condensate may collect in a sump below the sorbent trap. These condensates should be added to the extract obtained from treatment of the sorbent resin with methylene chloride.

The particulate matter collected in the cyclones and on the filter of the sampling train should be examined microscopically for evidence of intact crystalline species whose identity might subsequently be obscured or lost in the ensuing separation treatments. Optical microscopy may be usefully combined with x-ray and/or electron diffraction and other microscopic analysis techniques wherever the examination of individual particles may be deemed appropriate in the general analytical scheme. After microscopic examination, the particulate catch will be extracted with methylene chloride or other suitable solvent and the extract, together with that from the sorbent trap, submitted to analysis by the general scheme outlined in Figure 1.b. for organic liquids. The residue, which may contain insoluble organic as well as inorganic components, should be subjected to analysis by infrared (IR), thermogravimetric analysis (TGA) and by high resolution mass spectrometry (HRMS), using a "probe" sample insertion technique.

Samples collected from liquid streams, most of which are likely to be aqueous and destined for dilution into groundwater, may be sampled batchwise or by continuous contact of a diverted side stream with a solid sorbent or a continuous extractant. As shown in Tables 1 and 2, the liquid sample may preferably be analyzed directly for some organic components, but for most purposes, filtration (to remove suspended solids), followed by extraction in an immiscible solvent such as methylene chloride will be the method of choice for preparing the sample for organic analysis. In any event a separate batch sample should be taken initially, which will be purged with a nonreactive gas to remove and collect low-boiling organic gases. This collected gas sample is then to be analyzed by GC/MS, similarly to the "grab" sample taken from a gaseous stream.

After filtration, the liquid filtrate of an aqueous sample should be extracted with a suitable organic solvent such as methylene chloride, having first been adjusted to a high pH and then to a low pH to promote extraction of partially dissociated ionic substances. Alternatively, contact of the aqueous filtrate with a sorbent resin may prove to be a preferable general method to remove organics which may subsequently be desorbed by a suitable solvent. In either case, the organic extract will then be subjected to analysis as shown in Figure 1.b. above, and the residue will be analyzed by gel-permeation chromatography (GPC) and HRMS (probe) to detect and identify any organics that were not able to be extracted or sorbed. Any solid residue that remains after filtration of a principally liquid sample will be analyzed in the same way as particulates removed from a gaseous stream, i.e., by microscopy, extraction with an organic solvent, and TGA, IR and HRMS analysis of the non-extractable residue.

Solid samples, which are likely to be particulate, and which may contain small amounts of entrained liquids, will be analyzed in the same manner as the solid particulate fractions removed by filtration from gaseous samples and liquid samples. The organic extracts of these samples can be expected to dissolve and remove any entrained organic liquids as well as the soluble portion of the solids themselves. These extracts will then be analyzed in the same manner as all other organic extracts.

The general analytical scheme for organic extracts, rinse solutions and other organic liquids is shown in Figure 1.b. When the information sought is not limited to a specific question about one or a few components, but requires instead a broad-ranging examination of the entire organic composition of the sample, an initial survey analysis should be performed prior to the application of various chromatographic separation techniques. Data may be obtained from TGA, IR, MS, GC and microscopic examination of residues remaining upon evaporation of the solvent (typically methylene chloride or similar low-boiling solvent) at a temperature not above 40°C. These data, in combination with NMR, which requires that a portion of the sample be redissolved in an appropriate solvent (aprotic for proton-NMR; ^{13}C-depleted for ^{13}C-NMR, etc), will serve to show what the general composition of the sample is, whether it is especially complex or limited to a relatively small number of components, and whether it contains high-molecular-weight and/or non-volatile organic species which might not be seen in a TCO assay. Any other relevant data, including that from a prior Level 1 study, should be considered here in the interest of developing the most efficient and productive plan for the subsequent separation and identification scheme.

On the basis of the survey analysis, a decision can be made as to whether a significant fraction of the sample appears to be of such low volatility that it will not be susceptible to analysis by GC/MS. If so, the entire sample should first be subjected to gel-permeation chromatography (GPC) to separate the high-molecular weight fraction, which is likely to contain many or all of the non-volatiles, from the relatively low-molecular-weight substances. A break-point of M.W. $\simeq$ 300-500 is likely to be satisfactory this separation. The high-molecular weight, non-volatile fraction is likely to be analyzed most successfully by a combination of NMR and IR (both Fourier-transform-assisted) and perhaps by HRMS, using a solids probe for sample insertion.

If the low-molecular-weight and relatively more volatile fraction from the GPC separation (or the entire sample if GPC was not required) appears to be a mixture of only a few substances, as suggested by the survey data, GC/MS may be sufficient to provide all the identification and quantification required. If not, then an LC separation, using silica gel, alumina or Florisil, as appropriate, will be necessary to resolve the mixture into more manageable fractions, as well as to assist in characterizing chemical composition. Chapter V of this manual provides a more detailed discussion of liquid chromatographic techniques that will be most appropriate to this operation.

Non-polar and aromatic fractions of the LC eluate may be submitted directly to GC/MS. Those that are more polar and acidic may benefit from a more discrete resolution of their components by means of high performance liquid chromatography (HPLC). The choice of a favorable combination of column packing, mobile phase and detector will depend in part on information available to the analyst about the sample at this point in the process and partly on the analyst's own experience and preference. Since HPLC techniques are often capable of resolving individual chemical substances, discrete fractions may be collected for subsequent analysis by HRMS. (FT) NMR. and/or (FT) IR, or by GC/MS. More detailed descriptions of these analytical techniques, with particular reference to their applicability to environmental assessment studies, are provided in Chapter V of this manual.

IV. SAMPLING METHODS

Sampling methods for use in Level 2 may in many cases be the same as those used in Level 1. In some cases where a specific measurement is sought, it may be possible to use simpler procedures than those prescribed for Level 1. In some cases, alternative procedures will be desirable to measure species not represented well by the Level 1 scheme and/or especially reactive compounds, such as certain reactive olefins, hydrazines, etc.

The available sampling methods have been described in detail in several sources. All of the Level 1 sampling methods and procedures are described in the "IERL-RTP Procedures Manual: Level 1 Environmental Assessment". (3) A companion document, "Technical Manual for Process Sampling Strategies for Organic Materials", (4) gives further details on Level 1 methods and additional methods that may be appropriate to Level 2 and Level 3 studies. Many specific methods are detailed in various ASTM documents, and the Federal Register contains descriptions of standardized EPA methods. The reference "Standard Methods for the Examination of Water and Wastewater", (20) and the EPA publication, "Handbook for Monitoring Industrial Wastewater" (21) are excellent resources for water sampling and analysis methods. Fugitive sampling methodology has recently been addressed in several EPA publications. (8a, 8b, 8c). The reader should refer to these and similar sources for detailed descriptions and discussions of specific methods. Those procedures which seem to be most appropriate for Level 2 studies will be reviewed briefly in this chapter. The orientation in selection of methods for consideration was influenced by the existing Level 1 procedures and the chemical categories represented in the MEG list of organic compounds.

Although it is possible and desirable to specify a restricted set of procedures for Level 1 studies, the Level 2 situation is not analogous. The objectives of studies at Level 2 may cover a wide range and may vary from the need for better process (flow) data to compound-specific emission or composition data. A set of methods must be put together for the Level 2 study which are most appropriate for each specific task. Generally speaking, it should be possible to choose from the sampling methods described in this Manual, although it may be desirable in some cases to make modifications of the procedures. Methods for some species are not yet well developed and will need to continue to evolve as the state-of-the-art advances.

Sources to be sampled may be organized by procedures into:

a) fixed sources: process and effluent streams, vents and stack emissions, and
b) fugitive emissions.

The sources will yield the basic sample types described as:

gas/vapor
particulate
liquid/slurry
solid

For the purposes of this Manual, particulates will be treated separately from the gases and vapors, although "particulate" refers to solid or liquid materials entrained in gaseous streams. Fugitive sources of particulates and vapors/gases are treated separately. Level 2 procedures for reactive compounds are also treated in a separate section.

A. Gases and Vapors

1. Gases

The Level 1 procedure for gases involves sampling (in a bulb) followed by on-site GC analysis. Gases are considered to be those species having boiling points within a range similar to those of the C_1 - C_7 hydrocarbons, i.e., -160°C to 100°C. Special provision is also made to measure the reactive reduced sulfur species on the on-site GC, using the FPD.

The disadvantage of the Level 1 procedure for the low-boiling materials is that qualitative chemical information cannot be obtained beyond that which might be inferred from the retention time data. Exoneration of a source on the basis of such limited information would require a risky assumption in many environmental assessment studies of sources of unknown composition. As an alternative, most compounds in the low boiling range, with the exception of certain reactive species, may be readily and reliably identified and quantitatively estimated by GC/MS analysis methods. The question then is of the most appropriate method for collecting the gas sample for the GC/MS study. At this point, it should be noted that experience with the Level 1 procedures -- both in terms of materials collected efficiently on the XAD-2 module and those lost in sample treatment steps -- suggests that all species boiling in the range of -160°C to 100°C (C_1- C_7 hydrocarbon equivalent) should be treated as gases.

In terms of the analysis method detection limits, it will be sufficient for Level 2 purposes in most cases to analyze the equivalent of 0.1 - 1.0 L of gas sample. It may be possible to collect grab or time-integrated samples in inert bags, as suggested by Figure 2. The bag could then be returned to the laboratory where it may be analyzed either directly or by preliminary concentration of the species on a material such as Tenax GC and subsequent thermal desorption. There are

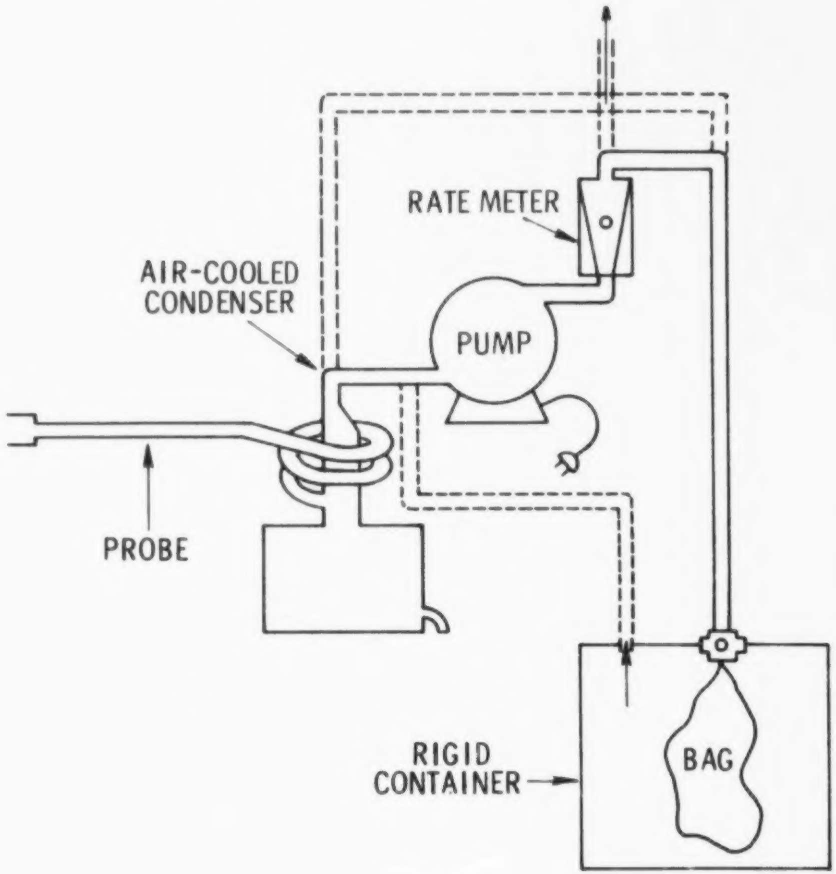


Figure 2 Integrated gas sampling train (Solid lines showing normal arrangement, Dotted lines - alternate arrangement, evacuating chamber around bag).

Source: EPA-600/2-76-122, April 1976 p.60

reports of the successful use of this method. The need to concentrate the samples will be set by the concentration of the species present in the sample and the detection limits of the analytical instrumentation. The major uncertainty with this approach is of the stability of the bag samples.

A comparative study of gas storage stability in two types of sample bags and glass bulbs carried out under the Arthur D. Little, Inc. program (22) indicates that glass bulbs are the best overall choice. Reactive and highly-polar materials were preferentially lost in the sample bags. Relatively simple (unreactive) gases were quite stable in the sampling bags and the bags are recommended for these type of species. In using sampling bags care should be taken to note the possible need for conditioning of the surfaces. Collection of high concentrations (> 1%) of organic gases in bags will usually lead to contamination which will adversely affect any of those bags.

An alternative method for sampling low molecular weight organic gases is the use of porous polymers. Two materials in particular, XAD-2 and Tenax-GC, have been used successfully for this purpose. The choice of methodology depends on the sampling temperature, trap size and the elution volume (Vg - the volume of gas in which the compound "breaks through" the trap) of the compound. If the higher-boiling end of the volatile range (e.g., B.P. = 0°C - 100°C) is being examined, or if the concentration of volatiles is high (allowing, therefore, lower volumes of sample to satisfy the analytical detection limits), then a simple sampling system as shown in Figure 3 could be used. Tenax-GC would be the adsorbent of choice in this sampler because its higher thermal stability would facilitate direct thermal desorption and analysis. In order to obtain adequately representative quantitative data for the stream, several 0.1 - 1.0 L samples should be collected. Larger samples may be needed if greater sensitivity is demanded. (See discussion in next section, "2. Vapors," for criteria in using sorbent resins.)

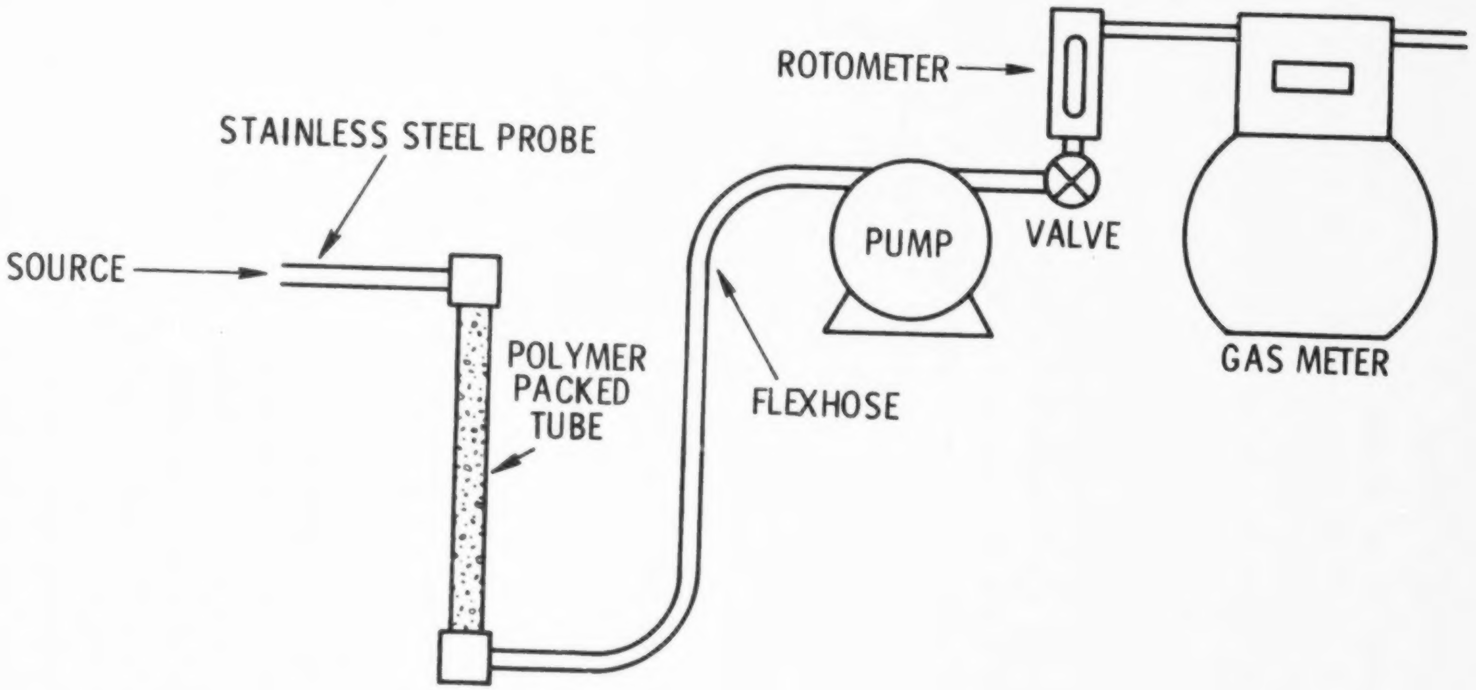


Figure 3 Porous polymer vapor sampling method

Source: EPA-600/2-76-122, April 1976 p.66

If the Vg value for solid sorbent sampling is too low at ambient (20°C ± 5°C) temperatures, then an approach using the Kaiser tube thermal gradient on a porous polymer might be used, as shown in Figure 4. While this approach has great promise from a theoretical viewpoint, preliminary field treatments have met with limited success, due to difficulty in maintaining a uniform, high temperature gradient across the Kaiser tube.

No good procedures for concentration of sufficient quantities of gaseous species for biotesting have been identified. The best procedure currently available is the collection of the 3 x 500-liter bag samples, which is the sampling method required for the "stress ethylene" test.

2. Vapors

In the context of this report, vapors are defined as compounds with boiling points above about 100°C (equivalent to a C_8 normal hydrocarbon) that exist as gaseous species in the stream or environment to be sampled because they are present below their equilibrium vapor pressure concentrations. When these same species are present at concentrations above their vapor pressures they would, of course, exist as aerosols and be sampled as particulate. Most of the compounds in the vapor range are sampled efficiently by the XAD-2 sorbent module (Figure 5) in the SASS train (Figure 6).

The preferred Level 2 sampling procedure for organic (and organometallic) vapors is the use of XAD-2 or Tenax-GC. Alternative methods should be used only when there are data to show an established preference over these two materials. The resins can be used with the sorbent module of the SASS train alone (no particulates, no impingers) when sufficient quantities are required for biotests. XAD-2 is the preferred resin when solvent extraction procedures are to be used in sample preparation. If thermal desorption is to be used, Tenax-GC is the sorbent of choice. Thermal desorption methods should generally be reserved for small-scale sampling apparatus. While XAD-2 and Tenax-GC

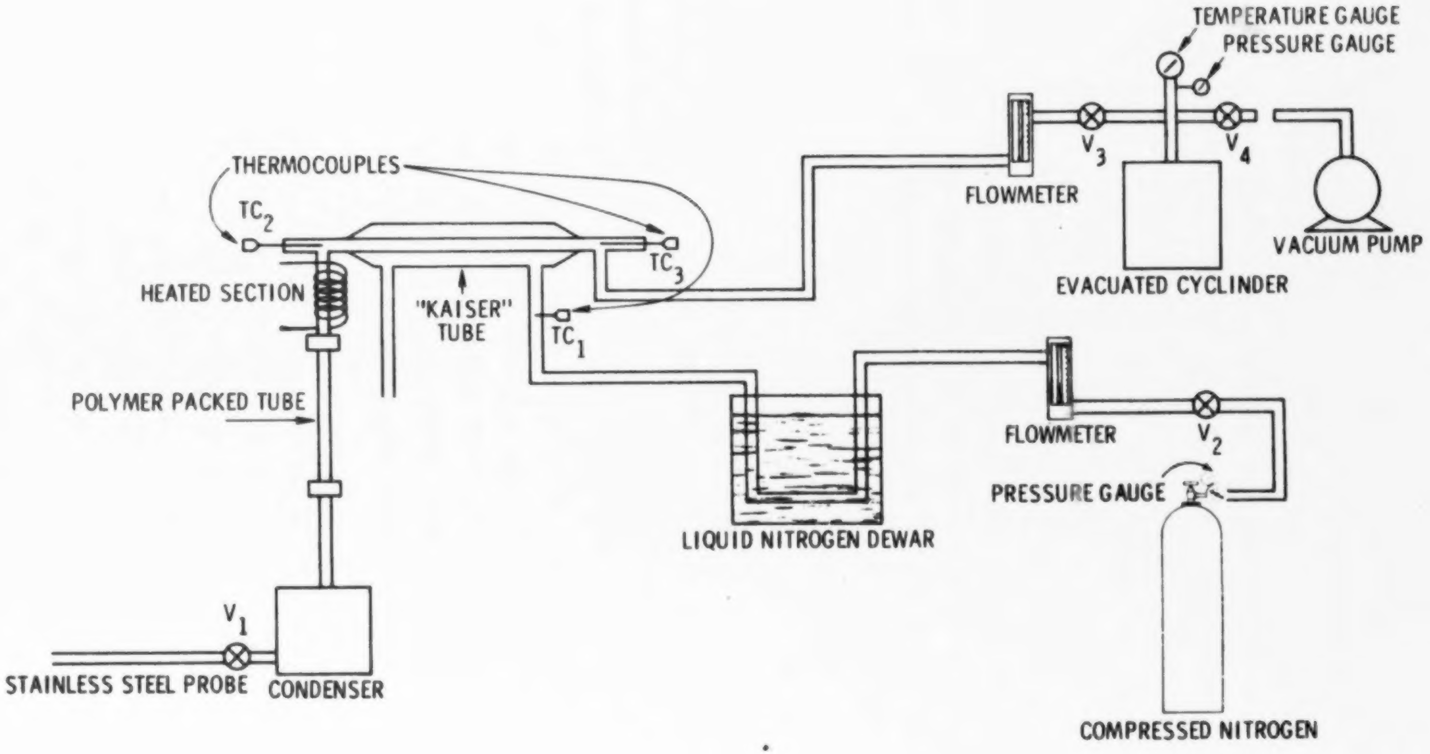


Figure 4 Porous polymer and thermal gradient sampling train

Source: EPA-600/2-76-122, April 1976 p. 28

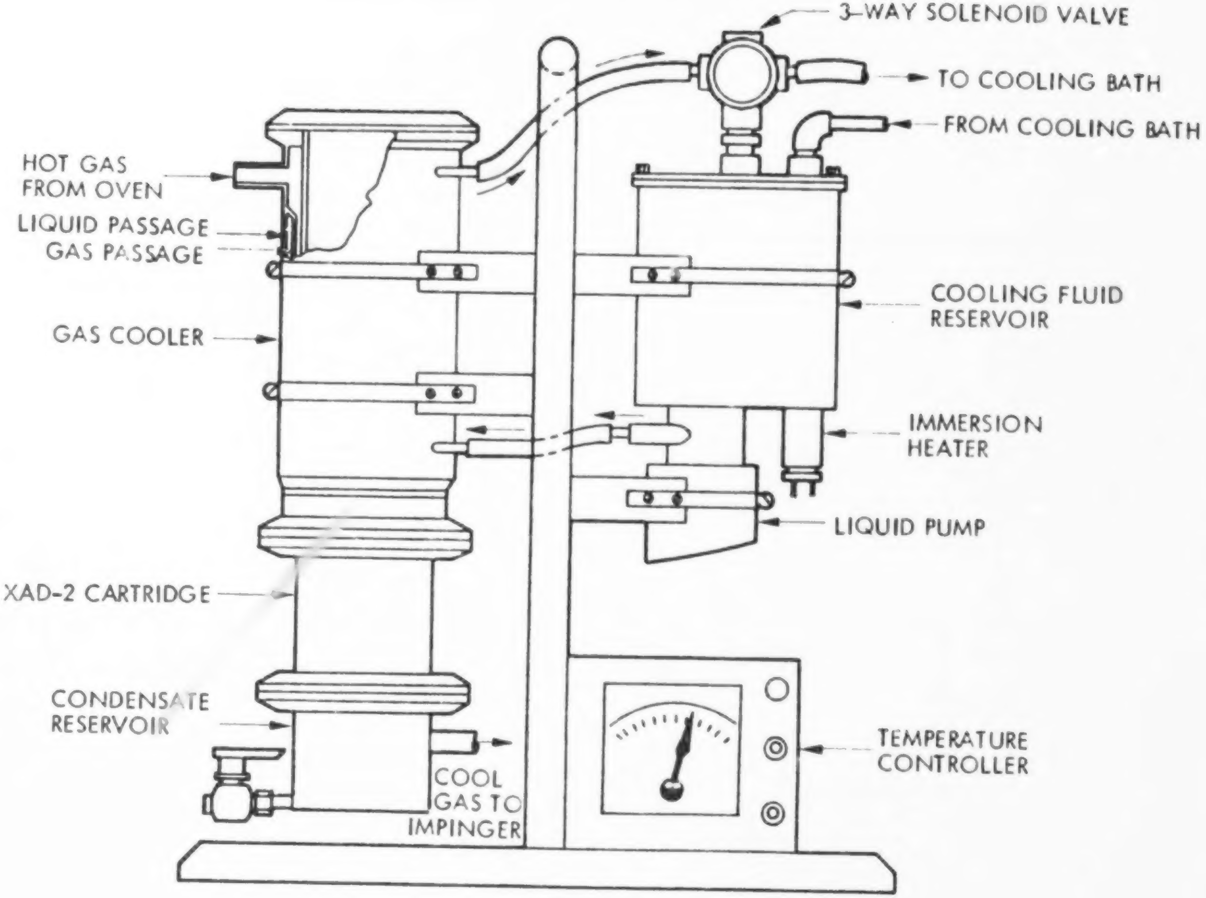


Figure 5 XAD-2 Sorbent Trap Module

Source: EPA-600/2-76-160a, June 1976 p. 32

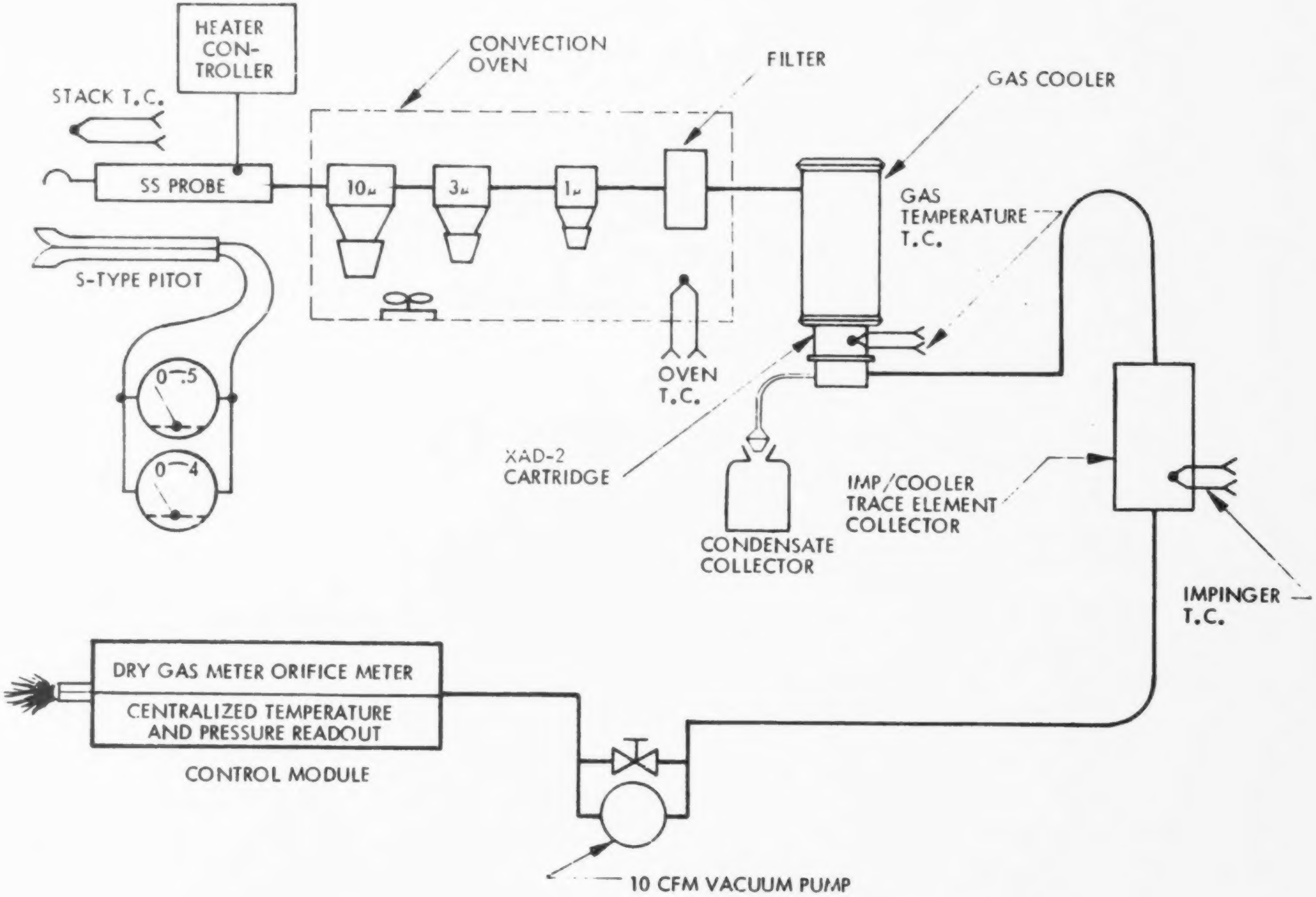


Figure 6. Source Assessment Sampling Schematic

Source: EPA 600/2-76-160a, June 1976 p. 30

have comparable collection characteristics at 20°C, XAD-2 has generally slightly better volumetric capacity and has substantially greater (10X) weight capacity than Tenax-GC.

In many Level 2 cases it will be possible to use simpler sampling methods than the SASS train when only organic vapors are to be measured. In earlier studies reported in the literature, impingers and bubblers using toluene, xylene, isooctane or ethylene glycol have been used to sample, for instance, PCB's and pesticides. NIOSH methods use activated petroleum-base charcoal and activated coconut-base charcoal for a wide range of compounds. Many other resins related to XAD-2 and Tenax GC have also been studied. (6)

Smaller scale versions of the SASS sorbent module have been successfully operated on modified Method 5 trains as with the Battelle Sampler (23) and in recent studies of incinerator emissions (24) in which the version shown in Figure 7 was used. Sufficient quantities of vapors for analysis may frequently be obtained by the simple version of a train previously shown in Figure 3.

The characteristics of XAD-2 and Tenax-GC for use in collection of vapors and quantitative data describing their collection efficiency and capacity are given in two EPA reports, "Selection and Evaluation of Sorbent Resins for the Collection of Organic Compounds" (6) and "Characterization of Sorbent Resins for use in Environmental Sampling." (7) For any given sampling situation, the quantity of resin to be used, volume to be sampled, operating temperature, etc., should be selected using the background provided in these reports.

Two basic factors control the quantitative behavior of these resins in a sampling system, their weight capacity and the volumetric capacity (Vg) for each compound with its specific volatility (boiling point) and polarity. If the resins are to be used for streams with high concentrations of pollutants (>> 100 mg/m^3), the capacity of the resin for the pollutant is a complex

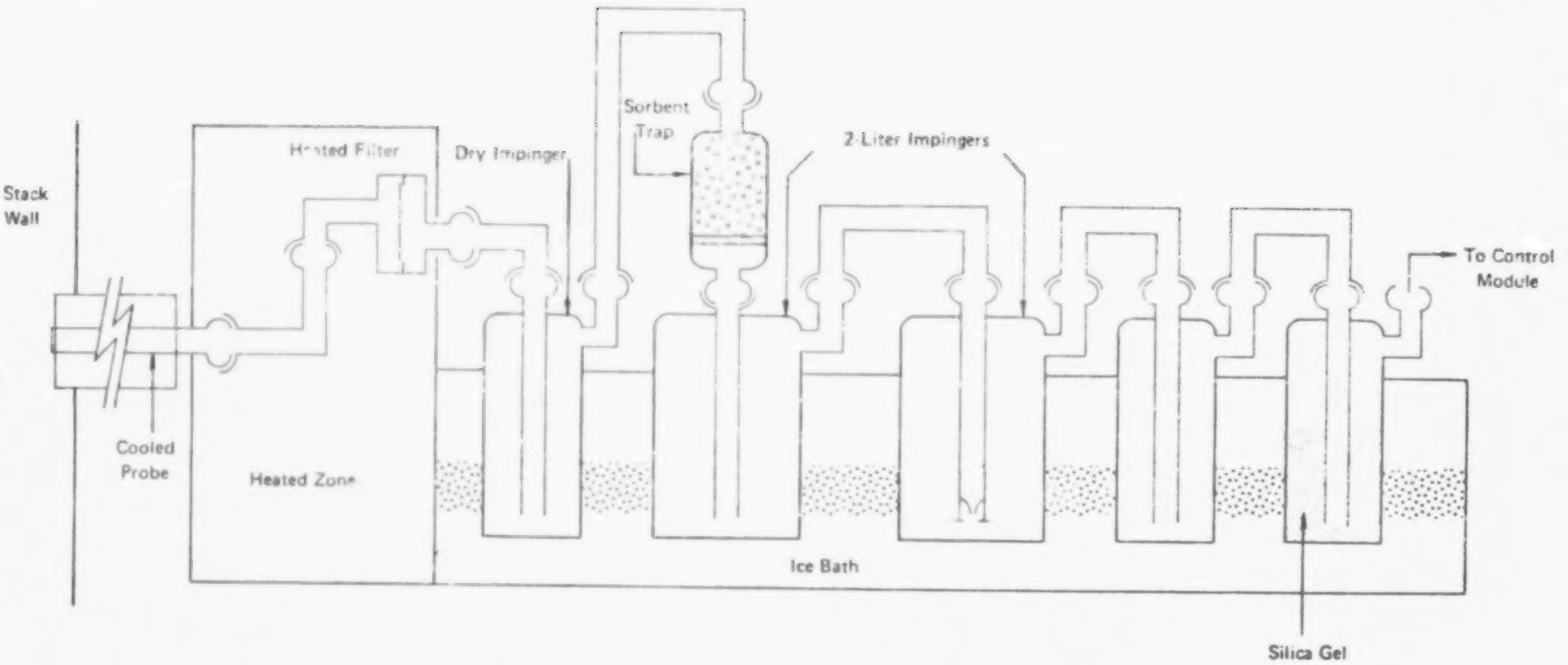


Figure 7. Method 5 Train Modified for Collection of Organic Vapors

Source: "Destroying Chemical Wastes in Commercial Scale Incinerators". Facility Report No. 5 EPA Contract No. 68-01-2966 TRW Systems Inc., Subcontract No. A82870 DNB-L, Arthur D. Little, Inc. July 1977 p. 14

function of pollutant concentration, volalitity and polarity. Generally speaking, XAD-2 will have an upper weight sorption capacity of 1 - 10% of the resin weight. Tenax-GC weight capacity is generally about 10% of that of XAD-2 or 0.1 - 1% of the resin weight.

Most environmental assessment studies involving the collection of vapors will represent situations where the pollutant concentration is quite low (e.g. 1 - 100 mg/cu m). In these cases, the principal characteristic influencing resin quality and sampling conditions is the volumetric capacity (Vg) for the specific pollutant. The volumetric capacity (Vg) describes the breakthrough capacity of the resin (in units of mL/g) and is the maximum volume of sample stream which can be pulled through the resin while still quantitatively retaining the pollutant.

A summary of the Vg values obtained for a large number of pollutants in the work described in Ref. 7 are given in Appendix C. The general behavior of the resin-pollutant interaction can be conveniently summarized in terms of an empirical correlation observed between elution volume (actually log Vg) and boiling point as shown in Figure 8. As is indicated in the Figure, good correlations were observed between log Vg and the boiling point within each compound category studied. There are some significant differences in Vg values for compounds that have the same boiling point but are in dissimilar compound categories.

These data can be used in two basically different ways starting with either the resin quantity or the volume to be sampled as the fixed quantity. The following examples describe the procedures used in designing the sampling approach.

Suppose a source were to be sampled for chlorobenzene and a typical set of Method 5 conditions were to be used, i.e., 28 Lpm for 1 hr. The Vg for chlorobenzene (Appendix C) on XAD-2 is 2.4×10^5 mL/g. Since total volume of 1680 L is to be collected, a minimum of 7 g of XAD-2 would be required for complete collection.

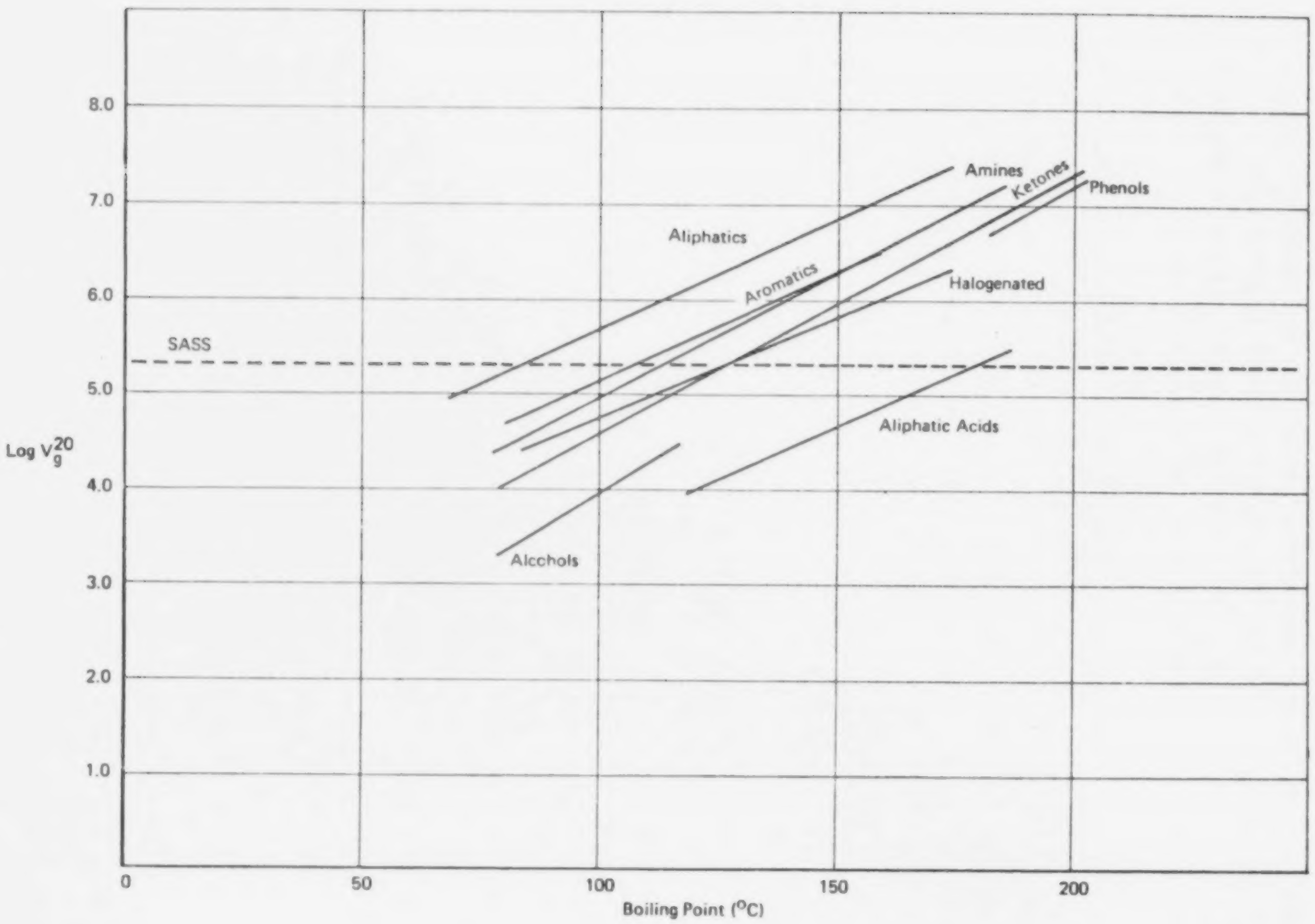


FIGURE 8. LOG V_g^{20} VS. BOILING POINT FOR INDIVIDUAL ADSORBATE GROUPS ON XAD–2

Another question might be whether or not the SASS train under standard conditions will quantitatively collect, for instance, benzyl amine. The sorbent cartridge in the SASS train contains about 130 g of XAD-2 and a 30 m^3 sample is normally collected. These values can be used to calculate a "cutoff" Vg value for the SASS train of 2.3 x 10^5 mL/g or log Vg - 5.4. This value is indicated by the dashed line in Figure 8. In order for a compound to be collected completely by the sorbent module its Vg would have to be greater than 2.3 x 10^5. The Vg for benzylamine is 7.9 x 10^6 and it would thus be completely collected. A comparison of several sampling trains relative to vapor collection was given in Table 2.

The compound categories studied as represented in Figure 8 cover each of the different types to be encountered well enough so that one can estimate a Vg (log Vg) value for any new compound by careful interpolation and extrapolation.

Two cautions are given when using the Vg data to estimate sampling requirements or to estimate efficiencies. The Vg values were obtained under laboratory conditions and any estimates for purposes of sampling system design should be decreased by about a factor of two as a safety margin. The Vg values have a normal temperature dependence and careful temperature control is necessary when operating near the boundaries of the trap limit. The Vg values given in Appendix C and Figure 8 are all for 20°C, the design temperature of the SASS sorbent module. A 10°C change in sorbent module temperature will result in a change in Vg value of about a factor of two.

"Normal" care (as specified in Federal Register Method 5) should be taken in both gas and vapor sampling to obtain a representative sample. There is no explicit Level 2 requirement for isokinetic sampling of gaseous species, but sampling should either be taken across the cross section of the duct or in a well-mixed portion of the stream.

B. Particulates

Particulates consist of solid and liquid aerosols; both are collected efficiently by appropriate combinations of cyclones and filters. Other special purpose particulate collectors such as electrostatic precipitators have found limited application in the collection of samples for environmental assessment studies related to chemical composition.

There is a wide variety of trains and configurations that can be used to characterize particulate emissions. Many of these have been summarized and reviewed in the EPA report, "Technical Manual: A survey of Equipment and Methods for Particulate Sampling in Industrial Process Streams" (10). The SASS train is described in detail in the EPA report, "Source Assessment Sampling System: Design and Development." (25).

For chemical characterization studies and to provide samples for biotesting, the SASS train shown in Figure 8 is used for Level 1 studies. The SASS is capable of providing particulate sample in the following size ranges:

> 10 μm	cyclone
3 - 10 μm	cyclone
1 - 3 μm	cyclone
< 0.5 μm	filter

The first two and last two size ranges are each combined to yield only two particulate fractions for analysis in Level 1 but can be maintained separately for Level 2 studies. Interest in analysis of each of the size fractions might be related to the relative distribution of the trace metals or pesticides or other species of interest.

For simple quantitative measurement of total particulate emission levels, or if smaller quantities of particulate are required, the Method 5 train (Figure 9) as described in the Federal Register may be adequate.

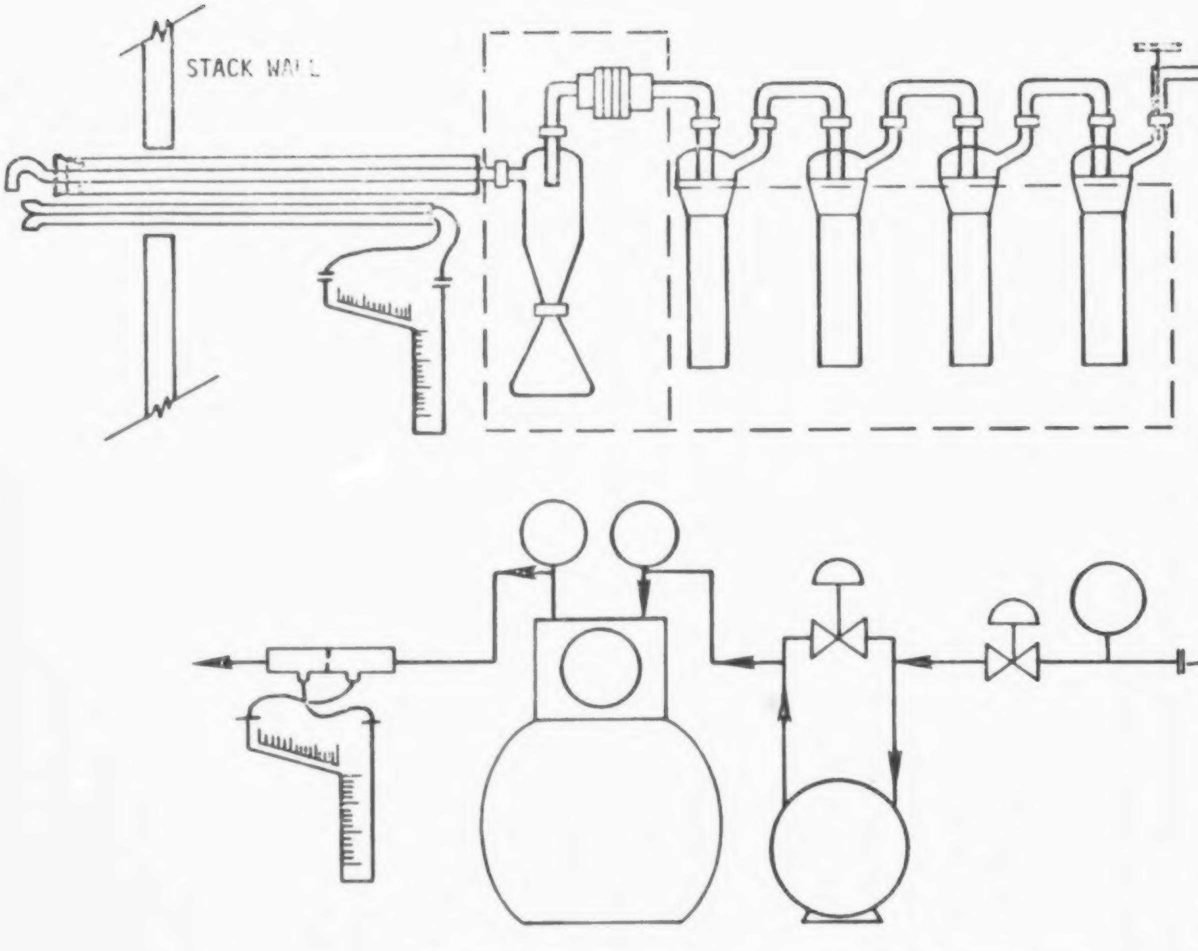


Figure 9 Method 5: Particulate Sampling Train

Source: 40 CFR 60, Appendix A - Government Printing Office, Washington D.C., July 1976

Particle sizing studies may be done with both impactors and cyclones. Most previous studies have been done with impactors of the Anderson and Brink type. Present evidence indicates that cyclones are preferred for particle sizing devices because they are less subject to operator errors than impactors and provide sufficient sample of sized particles for analysis. A five-stage series cyclone system has been designed which allows in-stack sampling.

A small electrostatic precipitator is under development and may prove useful as a replacement for the backup filter used in sizing devices. These devices could allow longer sampling times in situations where rapid buildup of material on the filter would otherwise require premature conclusion of sampling.

C. Liquids/Slurries

The general considerations given in the Level 1 Procedures Manual still pertain for Level 2 sampling of liquid and slurry streams. Stream homogeneity and flow rate are important factors to consider in collecting a representative sample and may be accomplished by a number of well established methods (4).

Grab samples, such as collected in the Level 1 Procedure, may also be used for Level 2 studies. Grab samples will be adequate if the primary Level 2 objective is more complete qualitative chemical or biological characterization than provided in Level 1. However, it is expected that most Level 2 studies will also require better quantitative data and for this purpose proportional sampling should be used. Sampling may be done proportional to either time or flow, and the choice will have to be dictated by the process characteristics and the measurement objectives. It is possible to obtain samplers which provide the substance in a composite or separate sequential mode. Sampling with this type of equipment would be restricted to streams with low or no visible solids. Slurries should be sampled by grab techniques.

For aqueous streams, grab sampling combined with solvent extraction of organics is a tedious procedure and does not always lead to quantitative extraction. Continuous extraction/concentration techniques used in conjunction with a proportional sampler offer significant promise for obtaining a quantitative time-averaged sample from aqueous liquid streams.

The Carbon Adsorption Method (CAM) has previously been used by EPA in a large number of water and wastewater sampling studies. While the CAM has apparently good extraction efficiency, quantitative recovery of some compounds is poor. Recent studies in the laboratories of EPA (26) and ERDA (27) indicate that XAD-2, XAD-8 and combinations of these resins are good sorbents for the extraction and recovery of ppb-level materials. A program is currently underway on the design of a XAD-2 sampler for use in the field collection of samples.

For high concentrations of organics in water (> 10 ppm) solvent extraction procedures are still recommended. The resins have limited mass capacity and are probably inferior to solvent extraction at high concentration levels.

For Level 2 studies, it is recommended that a separate liquid sample be collected for the analysis of volatile constituents. These volatile species, or "purgeables" have been the subject of recent EPA studies, (28) and this class has been shown to contain many compounds suspected as carcinogens. A number of the compounds on the MEG list would be detected as purgeables in a water sample.

The EPA Cincinnati protocol for purgeables should be adopted for Level 2. This requires collection of a special grab sample sealed with a Teflon-faced septum and no head space. The sample should be analyzed by the "purge-and-trap" procedure of Bellar and Lichtenberg. (17)

D. Solids

Level 1 procedures call for the use of a shovel or borer to obtain a sample for biotesting and to determine composition. Level 2 procedures should more systematically address the method of obtaining a representative sample. There are two basic types of solid samples - a bulk sample and a moving sample. Bulk samples include coal piles, sludge disposal areas, etc. Moving samples come from transport systems such as conveyor belts or transfer points. A number of ASTM procedures describe acceptable means of collecting each of these sample types.

For bulk samples, ASTM D346-35, "Standard Method of Sampling Coke for Analysis", describes the basic techniques for shovel, coning and quartering methods and locating sampling points. ASTM D-1799-65, "Sampling Packaged Shipments of Carbon Black", provides a method for bagged or cartoned materials. ASTM C183-71, "Sampling Hydraulic Cement", describes discharge point sampling and a slotted tube sampler for hopper sampling. ASTM D-2013-72, "Preparing Coal for Analysis", describes several mechanical sample dividers and riffles which can be used in preparing a fraction of the sample for analysis.

Moving samples may be collected by several procedures. A "stop belt" method involves stopping periodically and removing a standardized portion of the stream, taking care to obtain a complete cross section, since settling will occur. A cutter device, as described in ASTM D-2234-72, removes a portion of the stream by a traverse at a uniform speed. Samples from discharge points may be collected by moving a pan across the entire cross section of the discharge.

E. Fugitive Emmissions

Fugitive emissions are all those emissions discharged to the environment by a source other than a well-characterized stack or stream. They may include particulate, vapor, gas and water samples or individual species. Fugitive emissions can be considered to be dilute source samples at ambient conditions. The dilution factor requires special consideration in sample volumes required for collection. The fact that fugitive emissions species are defined only as being present in the ambient environment poses special sampling strategy problems for sampler choice and location.

The general characteristics of fugitive emissions and sampling methodology have been described in recent EPA reports. (8, b, c.)

Airborne fugitive emissions may generally be described in terms of:

Site Source
Specific Source: Category 1
Specific Source: Category 2

Several examples of these are described in a worst case site description in Figure 10. A "site source" is a general emission contributed to by many individual sources. Sampling such a source requires an upwind/downwind strategy. Some specific diffuse sources, Category 1, can be sampled by placing a sampler directly downwind if it has minimum confusion by other sources. Other specific sources, Category 2, are less diffuse, such as hearth or coke oven vents, and may be sampled using point source sampling methods.

Particulate samples from site sources may be sampled using a Hi-Vol sampler. If size fractionation is desired, a Hi-Vol impactor stage may be added. For Category 2 specific sources, the same choices for stack methods described in Section IV.B. are applicable. Primary emphasis in a level 2 study may be on better quantitative data which will require collecting a large number of samples with associated meteorological and source data.

By operating at about 50 cfm the Hi-Vol sampler is generally capable of collecting sufficient fugitive particulate sample for study (chemical analysis). There is no analogous equipment or method for sampling fugitive gases and vapors. The ambient/fugitive concentrations are 100 - 10,000 times lower than source levels, but the currently

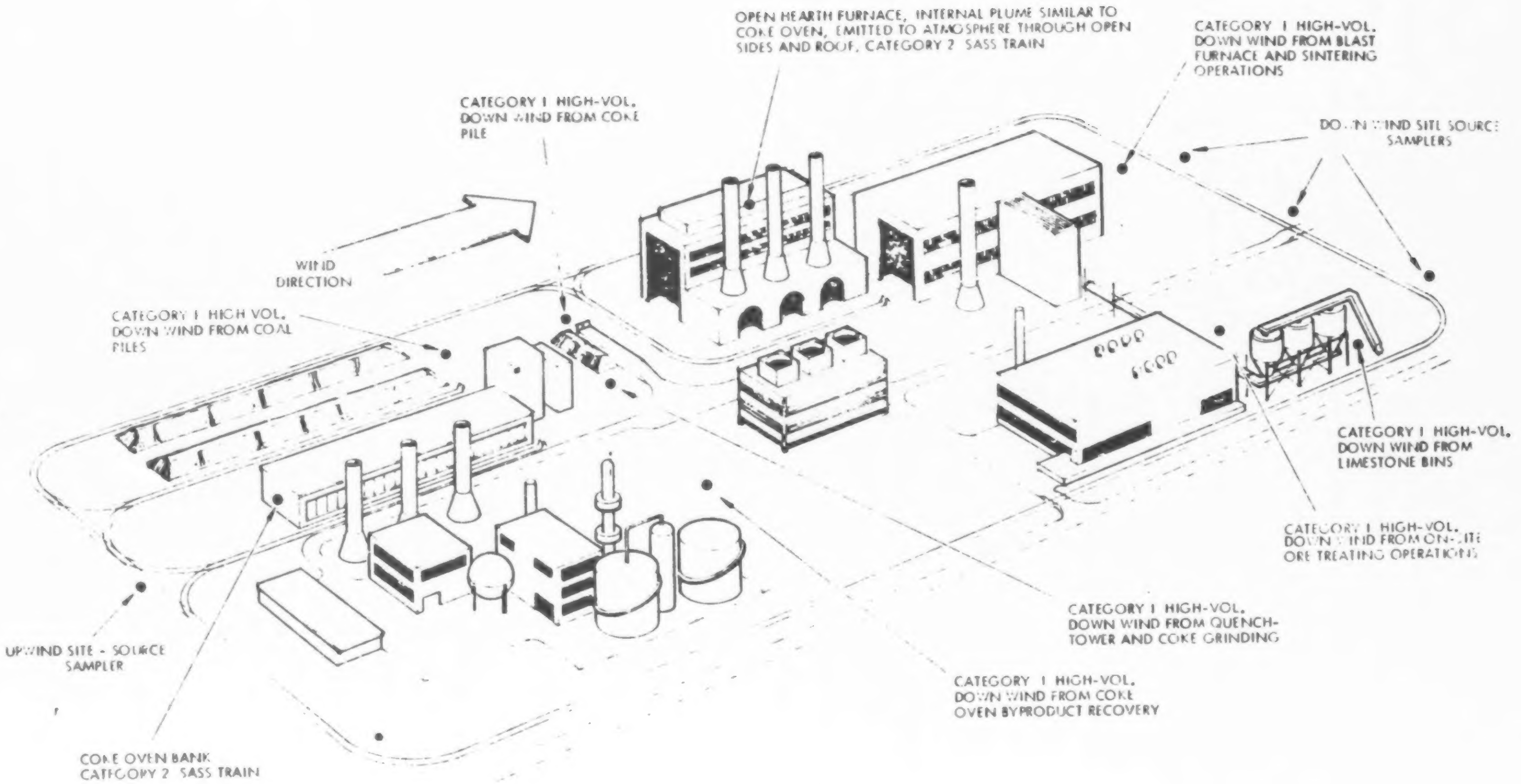

OPEN HEARTH FURNACE, INTERNAL PLUME SIMILAR TO COKE OVEN, EMITTED TO ATMOSPHERE THROUGH OPEN SIDES AND ROOF, CATEGORY 2 SASS TRAIN
CATEGORY I HIGH-VOL. DOWN WIND FROM BLAST FURNACE AND SINTERING OPERATIONS
CATEGORY I HIGH-VOL. DOWN WIND FROM COKE PILE
DOWN WIND SITE SOURCE SAMPLERS
WIND DIRECTION
CATEGORY I HIGH VOL. DOWN WIND FROM COAL PILES
CATEGORY I HIGH-VOL. DOWN WIND FROM LIMESTONE BINS
CATEGORY I HIGH-VOL. DOWN WIND FROM ON-SITE ORE TREATING OPERATIONS
CATEGORY I HIGH-VOL. DOWN WIND FROM QUENCH-TOWER AND COKE GRINDING
UPWIND SITE - SOURCE SAMPLER
CATEGORY I HIGH-VOL. DOWN WIND FROM COKE OVEN BYPRODUCT RECOVERY
COKE OVEN BANK CATEGORY 2 SASS TRAIN

Figure 10. Decision Example for "Worst Case" Site

Source: EPA 600/2-76-160a, June 1976 p.51

available methodology will not allow flow rate scaling to collect large quantities. Although there has been only limited testing, it is believed that the general bag and sorbent (Tenax GC) procedures described in Section IV A for source levels will provide sufficient sample for chemical analysis studies of fugitive vapors and gases. However, use of these methods for this purpose requires further careful validation.

A very high volume fugitive air sampling train (FAST) is currently under development at the Research Corporation for use in special studies. The FAST train is designed to operate at 6 cu m/min (180 cfm) for 8 hours. Particulate will be collected in the 0-3 μm and 3-15 μm size range and vapors will be collected in an XAD-2 module.

The same procedures described for Level 1 fugitive water sampling are recommended for Level 2 studies, if required.

V. ANALYSIS METHODS

A. Liquid Chromatography

In Level 2 organic analysis, as in Level 1, it will usually be necessary or desirable to perform some sample fractionation prior to analysis. One approach to sample fractionation is liquid column chromatography (LC) on media such as silica gel, alumina, or Florisil. An LC separation on silica gel is often useful as a method for separating a sample into a small number (i.e., 4-8) of fractions prior to bioassay or chemical characterization. A seven-fraction scheme of this type is used in Level 1 organic analysis and in many cases it may be possible to use those same seven fractions for further, Level 2 analysis. In other cases, in which discrete Level 2 samples have been collected, alternative fractionation procedures are likely to be attractive.

A number of different LC schemes will be used in Level 2, depending on which categories of compounds are of concern. Furthermore, since Level 2 analysis will ordinarily be directed towards only one or a few specific categories of compounds identified in Level 1, a simple two- or four-fraction LC separation may suffice.

Other LC procedures that are of value in Level 2 organic analysis are separations on alumina or Florisil to remove interferences in the analysis of selected substances. An example, shown in Figure 11, is the Florisil column pre-cleaning procedure used to remove interfering substances prior to analysis of polychlorinated biphenyls (PCB's) in industrial effluents (29). Another example of possible application of LC in Level 2 organic analysis is the use of Sephadex-LH, a gel permeation chromatography medium, which can be used for chemical class separation in a number of modes: lipophilic-hydrophilic partitioning, molecular size separation, and aliphatic-aromatic separation (30). For example, recent unpublished studies at Arthur D. Little, Inc., have indicated that Sephadex LH is superior to Florisil/alumina for clean-up of extracts prior to GC/ECD analysis of pesticides.

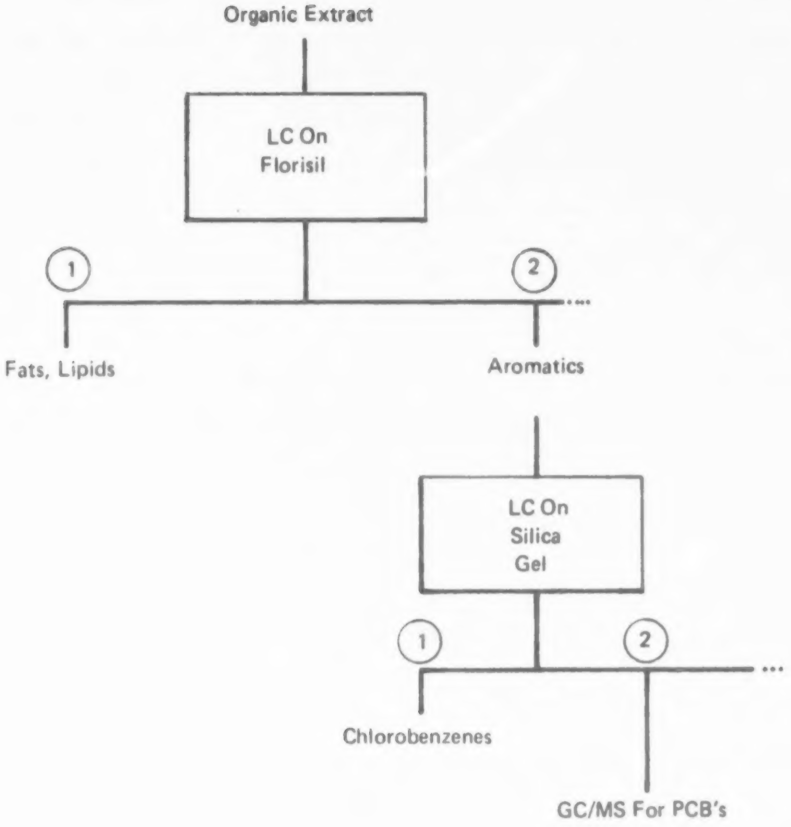


FIGURE 11. DIRECTED LEVEL 2 LC SCHEME FOR ANALYSIS OF POLYCHLORINATED BIPHENYLS

B. High Performance Liquid Chromatography (HPLC)

HPLC is a separation technique with applications in quantification, isolation and identification. HPLC is differentiated from other LC methods by high speed, high sensitivity and high resolution comparable to that of gas chromatography. These improvements have been achieved by columns using microparticle packings with small diameter (5-50 micrometers) and high surface area (approximately 300 m^2/g particles). Separations may be achieved by differences in molecular size, number or type of functional groups, steric configuration, polarity, etc.

1. Detectors

The two most commonly used methods of detection of sample components in HPLC effluents are ultraviolet (UV) absorbance detectors and refractive index (RI) detectors. Features of these two types of detectors are summarized in Table 6. High sensitivity and specificity are achievable using a UV detector at fixed (e.g., 254 nm) or variable (200-800 nm) wavelength. Lower limits of detection in the nanogram range have been reported for strongly absorbing sample species (i.e., molar absorptivity $\simeq$ 14,000).

The differential refractometer detector has lower sensitivity and less specificity than the UV detector. The RI detector responds to essentially all sample components and is a potential "universal" detector for HPLC, but lower limits of detection are in the microgram range. Furthermore, generality of the RI detector response requires matching of solvent system refractive indices during gradient elution HPLC; this is difficult to achieve in lab practice. Other types of HPLC detectors, such as the moving wire flame ionization detector and the fluorescence detector, do not appear to offer any special advantages for Level 2 organic analysis compared to the UV and RI detectors. The fluorescence detector might be applied in some specific cases, such as analysis of polynuclear aromatic hydrocarbons.

An HPLC-MS combination might be of interest in some Level 2 applications. However, these systems are not in common use because of the

TABLE 6

Comparative Specifications of HPLC Detectors

	UV	RI
Range of Application	Selective	Universal
Destructive or Nondestructive	Nondestructive	Nondestructive
Gradient Compatible	Yes	--
Detectability		
Min. Physical Change	2×10^{-4} Abs.	1×10^{-7} RI units
Minimum Concentration	4×10^{-9} g/mL	7×10^{-7} g/mL
Minimum Det. Sample	$\sim 2 \times 10^{-11}$ g/sec	$\sim 3 \times 10^{-9}$ g/sec
Linear Range	3000	3000
Short Term Reproducibility	Less than 1% deviation	Less than 1% deviation
Peak Shape	Positive only	Positive or Negative
Peak Spreading		
Nom. Response Time	1 second	1 second
Cell Void Volume	8 microliters	6 microliters
Experimental Upper Limit	46 microliters	20 microliters
Flow Sensitivity (b.l. shift 0-90 mL/hr)	12% f.s.	$\sim$25% f.s.

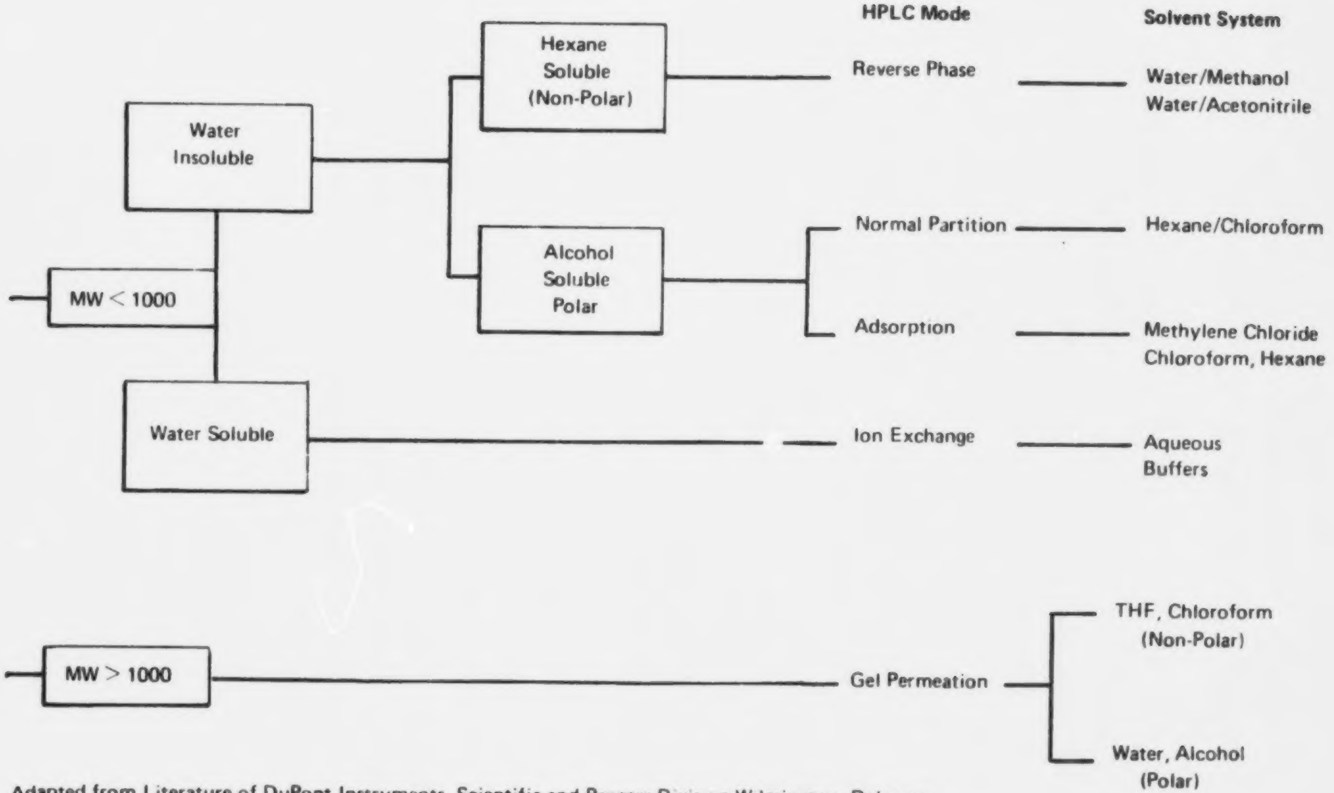
Source: Basic Liquid Chromatography, Varian Instrument Company formidable problems in designing an interface to remove carrier (solvent) prior to MS analysis. Similarly, the FTIR detector offers great promise when and if it becomes fully developed for this application.

HPLC methods are likely to be used in two different modes in Level 2 organic analysis. First, HPLC separations by gel permeation, normal, or reverse-phase chromatography are useful ways of achieving a preliminary coarse fractionation of the sample according to molecular weight range and polarity. Secondly, some normal or reverse-phase chromatographic procedures may be selected as the quantitative analytical finish for sample components that have high molecular weight, poor thermal stability, and/or high polarity. A guide to selection of an analytical HPLC method is summarized in Figure 12. In practice, of course, the use of such a guide would require that determination be made at each decision point to provide information required for the choice. The types of HPLC separations most useful in Level 2 organic analysis are discussed briefly below.

2. Gel Permeation Chromatography

This technique is based on separation by molecular size, which is closely related to molecular weight. Large molecules may be excluded from some or all of the pores in the column packing material, due to their hydrodynamic volume in solution. Therefore, large molecules elute from the column before smaller molecules which permeate the pores. Columns are available in a variety of nominal pore sizes, and a number of columns are usually used in series to ensure adequate resolution.

Column packings used with non-aqueous mobile phases (for example, tetrahydrofuran, toluene, dimethylformamide and methylene chloride) include polystyrene (e.g., Styragel), spherical silica (e.g., Porasil) and irregularly shaped silica (e.g., Merkogel Si). Packings suitable for use in aqueous GPC include Dextran gels (e.g., Sephadex) and controlled pore-size glass (e.g., CPC).



Adapted from Literature of DuPont Instruments, Scientific and Process Division Wilmington, Delaware

FIGURE 12. GUIDE TO SELECTION OF HPLC ANALYTICAL PROCEDURES ACCORDING TO CHARACTERISTICS OF SPECIES SOUGHT

GPC may be used to achieve initial sample fractionations on a fairly large scale, since 150 to 200 mg of material may be handled by μ-Styragel columns. Even higher loading capacities can be achieved by using larger particle sizes (macro-Styragel) and column diameters.

For purposes of Level 2 organic analysis, gel permeation chromatography (GPC) will probably be most useful as a technique to separate samples into two molecular size ranges, with a molecular weight of about 300-500 as the dividing point. The species in the lower molecular weight range can then be analyzed by gas chromatography or GC/MS, although some small and very polar or thermally unstable molecules (amino acids, etc.) may require derivation or alternative treatment. The sample components in the higher range will require analysis by methods not involving GC. These might include mass spectrometry (LRMS or HRMS) or Fourier transform infrared (FT/IR) or nuclear magnetic resonance (FT/NMR).

3. Reverse Phase HPLC

This technique is based on separation by polarity differences in the mobile phase vs. stationary phase. The stationary phase is prepared by using long-chain alkyl silylating reagents to produce a hydrophobic layer on a solid silica substrate. Non-polar solutes have a higher affinity for the stationary phase than do polar solutes. The mobile phase is generally programmed in a continuous gradient elution scheme from polar to non-polar solvents. Water/methanol and water/acetonitrile are binary solvent systems frequently employed. In reverse phase HPLC, polar sample components elute first.

In Level 2 organic analysis, reverse phase HPLC may be applied to low molecular weight range sample components to separate the polar materials, which would require derivative formation prior to gas chromatographic or GC/MS analysis, from the non-polar materials suitable for direct gas chromatography or GC/MS. Reverse phase HPLC is also an attractive possibility for ultimate quantitative analysis of some classes of compounds, such as phenols and carboxylic acids.

4. Normal Phase HPLC

This technique, like reverse phase HPLC, is based on separation by polarity. In normal phase separations, the stationary phase is more polar than the mobile phase. Gradient elution systems from non-polar to polar solvents are used, and non-polar solutes elute first. In Level 2 organic analysis, normal phase HPLC may be used as a quantitative analytical finish for some classes of compounds. The choice between normal and reverse phase systems for this purpose would be based on several considerations:

(1) Quantity of solute to be isolated for qualitative identification by NMR, IR, etc.
(2) Solute class solubility in the mobile phase.
(3) Column capacity for solutes in general.
(4) Ease of solvent removal after HPLC.

The first point is amply illustrated by considering the separation of polycyclic aromatic hydrocarbons. Excellent separations between these solutes is accomplished using H_2O/MeOH isocratic and gradient mixtures as solvents. With these solvent systems and a C_{18}-silylated silica support, even the isomeric pair of phenanthrene and anthracene can be partially separated. However, despite the excellent thermodynamic selectivity of this HPLC system, it is limited in the quantity of solute which can be chromatographed. This is due in part to the lower capacity of reverse phase packings, the normal loss in resolution with sample overload, but it is due primarily to the solubility limit of the hydrocarbon moiety in polar solvents. Using a hydrocarbon solvent in conjunction with a silica support (normal phase system) allows larger quantities of this particular class to be isolated (larger capacity of support, higher solubility, etc.) although the resolution is diminished. It should be noted that sample solubility in the mobile phase is of prime consideration in preparative chromatography, particularly when mild gradients (water to methanol, n-hexane to methylene chloride) are used in reverse or normal phase systems.

If HPLC is to be used to isolate large quantities of material, the column capacity becomes a factor. For example, semi-preparative reverse phase columns have a typical capacity of 5 mg while a micro-particulate silica gel for normal phase LC has a capacity of 1000 mg. It is therefore not always possible to simply scale-up an analytical reverse phase HPLC separation to achieve a preparative procedure.

It should also be noted that subsequent analytical procedures to be applied to HPLC fractions will possibly necessitate the removal of solvent from collected fractions. Water/methanol eluents can be more difficult to remove than a volatile hydrocarbon and may result in the loss of some of the analyte. From this point of view, normal phase would seem to offer some advantages.

C. Thermal Gravimetric Analysis (TGA)

The techniques which are used for the ultimate qualitative and quantitative Level 2 analysis will depend on the volatility of the sample components. Analytical procedures based on gas chromatography (GC), including GC/MS, are suitable for volatile components. Sample components that are non-volatile (because of high polarity and/or high molecular weight) must be separated and analyzed by other techniques. Thermal Gravimetric Analysis (TGA) is a rapid instrumental method for quantitatively determining the volatility of a sample as a function of temperature.

In a TGA analysis, the weight of a small sample (1-10 mg) is continuously recorded as a function of time (isothermal operation) or temperature (temperature programmed operation). The water content in mixtures, for example, may be determined by TGA by virtue of the well-defined weight loss at its boiling point. In addition, isothermal TGA can be used to determine residue on ignition on a micro scale by isothermal operation at high temperature. For sample characterization studies, temperature programmed operation is more normally used. The sample atmosphere (nitrogen, air, etc.) may be controlled to aid in the study, for instance, of decomposition of non-volatile samples.

An example of the applicability of TGA to Level 2 organic analysis would be the determination of whether "aromatic" material indicated as present in a source by Level 1 analysis is more suited to separation and analysis by GC/MS or by HPLC.

D. Gas Chromatography (GC)

Gas chromatography is a very powerful tool for separation of complex mixtures of organics with appreciable volatility. GC is also an exceedingly valuable technique for quantitative analysis of sample components. However, qualitative analysis by GC is limited to inferences drawn from retention times of individual peaks and known detector selectivities. (The combination of mass spectrometric detection with GC to give qualitative data is discussed in a separate section.)

1. Detectors

A considerable variety of detection principles have been utilized for gas chromatography purposes. Of the detectors available, there are three which are potentially of interest in Level 2 organic analysis.

The flame ionization detector (FID) is the most versatile general purpose device. The FID responds to any substance that will burn in the air/hydrogen flame to produce ions. Most organics, except for highly halogenated species, give strong FID responses. The lower limit of detection for organic species is on the order of one nanogram per microliter (ppm) of injected solution, and the dynamic range of the detector spans four or more orders of magnitude.

The electron capture detector (ECD) is specific for species that contain electronegative atoms or groups--halogens, phosphorus, sulfur, and nitro-groups. The high selectivity of the ECD has been used to good advantage in analyses of pesticides and polychlorinated biphenyls (PCB's). The lower limit of detection is as much as 1000 times lower than that of the FID, but the dynamic range is generally smaller. The magnitude of the ECD response is sensitive to analyte structure, as well as to concentrations, since different species have different electron capture cross sections.

The flame photometric detector (FPD) is specific for species that contain sulfur or phosphorus. Its specificity, detection limits, and sensitivity are comparable to those of the ECD, although a completely different principle of detection is involved. When operated in the sulfur mode, the FPD response is logarithmic, rather than linear, with concentration. The FPD may be utilized in Level 2 organic analysis of organophosphorus pesticides and some sulfur species (including on-site analysis of reactive sulfur gases, as in Level 1).

2. Columns

The number of potential choices of column type for Level 2 organic analysis is staggering. Columns may be packed, support-coated, open tubular (Scot) or wall-coated capillaries of stainless shell, glass, or Teflon. An enormous range of stationary phases is available, including porous polymers and liquids coated onto solid substrates. Highly specialized columns include the polyphenylether/phosphoric acid on Teflon matrix used for sulfur gases and the recent nematic phase liquid crystal packings used to achieve resolution of isomeric polynuclear aromatic hydrocarbons. These types of columns may be required in special Level 2 situations.

However, it appears that a set of five or six GC columns can be specified that will cover most Level 2 analysis requirements and would maximize comparability of data acquired in different environment assessment programs. A suggested set of columns for general purpose Level 2 work is the following:

- For volatiles - Oxypropionitrile/Porasil C (2 mm x 2 m glass). This column can separate hydrocarbons boiling between -161°C and 68°C in a single temperature-programmed run. Fairly high resolution within a narrower boiling range can be achieved by isothermal operation.
- For moderate volatility, non-polar species - Methyl Phenyl Silicone (SP 2250 or OV-17). (3% on Supelcoport or equivalent 2 mm x 2 m glass.) This stationary phase separates analytes primarily on the basis of volatility (boiling point) and can be used at temperatures up to 375°C. The liquid phase is a 50% phenyl silicone.
- For high boiling, non-polar species - Dexsil 400 (3% on Supelcoport or equivalent, 2 mm x 2 m glass). Dexsil 400 is a carborane-methyl phenyl silicone that is stable at temperatures up to 500°C. Like OV-17, Dexsil 400 is basically a boiling point column. It is useful for analyzing species such as the polynuclear aromatics. It does not function well much below 80°C.
- For moderately volatile and moderately polar species - Modified Carbowax 20M (SP 1000) (3% on Supelcoport, 2 mm x 2 m glass or stainless steel). Polyethylene glycol (Carbowax 20M) modified with a terephthalic acid, as in SP-1000, is a liquid phase suitable for analysis of a variety of moderately polar species including ethers, carbonyl compounds and alcohols. It can be used at temperatures up to 275°C.

In addition to these general purpose columns with broad applicability, unique, specially deactivated columns are required for Level 2 analysis of phenols and amines. Also, in some particular Level 2 studies it may be desirable to take advantage of the very high resolving power afforded by capillary column GC.

3. Gas Chromatographic Conditions

Details of gas chromatographic conditions, such as carrier gas and temperature regimes, will vary depending upon the compound categories of interest. In general, temperature programming will probably be required for Level 2 analyses.

E. Gas Chromatography/Mass Spectrometry (GC/MS/DS)*

The combination of gas chromatographic (GC) separation methods with mass spectrometric (MS) detection coupled with an automated data system (DS) is an extremely powerful tool for analysis of organic compounds. The GC/MS technique differs from other GC procedures discussed earlier in that GC/MS can provide specific qualitative information as well as quantitative data about sample components.

1. Detector

The detector in GC/MS is a dedicated low resolution mass spectrometer. This has the unique benefit of being both highly compound specific and having substantially uniform response to all components that are sufficiently volatile to pass through the gas chromatograph. Furthermore, under normally favorable circumstances, the MS/DS can discriminate among and often provide discrete quantitative data for two or more compounds that elute simultaneously from the GC. Lower limits of detection for conventional (non-capillary) column GC are typically 30-100 ng/μL of solution injected, and lower for capillary column GC.

The GC/MS combination has available a range of operating conditions that significantly affect the performance of the system. The operating parameters chosen must be appropriate to the objectives of each particular analysis if the optimum results are to be obtained.

The most significant choices concern the mode of ionization, and the format for mass scanning. Two classes of ionization mode are generally available: electron impact (EI) and chemical ionization (CI). EI provides energy in excess of that required for simple ionization, resulting in considerable fragmentation of the parent molecule. This fragmentation provides structural information and a characteristic signature for a given compound or compound class. Since reference spectra generally available are of the EI type, this ionization mode facilitates direct matching of spectra for species identification. For some compound types the fragmentation is so extensive that the parent ion is difficult or impossible to detect, making specific identification impossible. CI provides a much gentler mode of ionization, yielding fewer fragment ions and substantially larger parent ions. It is the method of choice for those classes that given no EI parent ion, such as the higher mass alcohols, or for those that give very small parent ions with less fragmentation; however, less structural information is provided, although some is available and may be of a unique type. Reactions with the CI reagent gas complicate the spectrum somewhat.

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*In this discussion, the term GC/MS is intended to imply also the existence of an automated data handling system which is a virtual necessity for Level 2 organic analysis.

A range of adjustments is available for both EI and CI, offering some intergradation of features. By varying the reagent gas composition, CI spectra can be made to approach the fragmentation pattern obtained in EI; reducing the electron beam energy in EI can simplify the fragmentation pattern of that mode. EI is somewhat more universal in application, as it provides a more consistent sensitivity from species to species, but CI can provide unique information that is sometimes necessary for identification. Both techniques can be used for the same material provided sufficient sample and time are available for multiple analyses.

The adjustable parameters in selection of a GC/MS mass scanning format are the range of the scan (or number of masses monitored) and the dwell time on each ion. These must combine to give a fast enough scan to yield several scans per GC peak; each complete scan must therefore last a few seconds at most. One alternative is to scan the entire (i.e., m/e 12 to m/e 600) mass spectrum of material eluting from the column at a frequency of about one scan every three seconds. However, the option of scanning the entire available mass range is normally chosen only if absolutely nothing is known about the sample. In virtually all Level 2 analyses, sufficient information will be available about the sample composition and/or the components of particular interest to allow one to scan a more limited mass range. For example, the mass scan could be limited to the range of m/e 100 to 300 if polynuclear aromatic hydrocarbons were the only compounds of concern. If a specific GC/MS analysis for PCB's was desired, a few selected clusters of masses corresponding to the di-, tri-, tetra-, etc., chlorobiphenyls could be monitored instead of scanning a continuous wide mass range. The extreme case of limited mass scanning would be to monitor a single ion continuously, if only one compound were of interest. Reducing the range of the mass scan allows an appreciably longer dwell time on each ion and this is used to improve the signal to noise ratio. A limited mass scan also enhances sensitivity by reducing background. The background elimination can also be effected in the data processing phase, but the dwell time for each ion is a real time parameter which is fixed during data acquisition.

The improvement in effective sensitivity can be as much as three orders of magnitude between the extremes of a complete mass scan and single ion monitoring. Limited mass range scanning of selected ions or clusters can approach the sensitivity of single ion monitoring.

The selection of the appropriate mass scan range will depend on the objectives of each particular Level 2 analysis. The presentation of the data accumulated in the GC/MS scans can also be varied according to the requirements of the analysis. One can print out a "reconstructed gas chromatogram" in which the sum of ions of all mass numbers for each scan is plotted versus mass spectrum scan number (a measure of retention time). A second alternative is to plot the data in the form of "mass chromatograms," in which only the abundance of selected ions, with m/e values corresponding to specific sample components, is considered. The mass chromatogram approach is especially useful for quantitative analysis of known components. In all cases, however, the quantitative data obtained from the selected ion mass chromatogram(s) must be supported by qualitative identification of the component producing the chromatographic peak(s). The confirmation of identity should be achieved by performing an initial

GC/MS run using a broad mass range scan (i.e., m/e 40 through the molecular weight of the component) and directing the data system to print out the mass spectrum of the scan(s) corresponding to the GC peak in question.

In interpreting the GC/MS results it is also important to consider retention time data as well as the mass spectra. If the MS data appear to show benzpyrene eluting ahead of phenanthrene from a Dexsil 400 column, it is reasonably certain that at least one of these compound assignments is incorrect. If reference samples of known components are available, absolute, as well as relative, retention times (RRT) can be used in interpreting GC/MS data. It is frequently beneficial to use internal standards, such as p,p'-DDI, for the purpose of establishing RRT's.

2. Columns

The discussion of gas chromatographic columns, which was presented above in the discussion of GC (Section D.2), holds equally well for GC/MS. The same four basic columns--Oxypropionitrile/Porasil C, SP-2250 or OV-17, Desil 400 and SP-1000, --are expected to be used for the bulk of Level 2 GC/MS work.

F. Mass Spectrometry (LRMS and HRMS)

There are two principal mass spectrometric techniques, in addition to GC/MS discussed above, that are applicable to Level 2 organic analysis. These are low resolution mass spectroscopy (LRMS) and high resolution mass spectroscopy (HRMS). Both of these techniques may be used extensively for analysis of non-volatile materials not amenable to GC. HRMS may also have application to various volatile materials as well.

1. Low Resolution Mass Spectroscopy

A low resolution mass spectrometer is typically capable of resolving differences in mass on the order of 1 part per thousand. This is equivalent to measuring individual m/e values to within ±0.1 to 0.5 mass units for the normal range of organic ions. An LRMS instrument is the type ordinarily used as a detector in GC/MS systems.

The use of LRMS data to determine the structure of single compounds is the mode of mass spectrometry that is most familiar in organic chemistry. As discussed in Section E (above), electron impact ionization, which leads to extensive fragmentation of parent (or molecular) ions is ordinarily used to generate spectra for comparison with library reference spectra. The library spectra may be in hard copy, (e.g., "Eight Peak Index of Mass Spectra," 1st Ed., Imperial Chemical Industries, Ltd., Mass Spectrometry Data Center, Alder Maston, Reading, United Kingdom, 1970) or in computerized data bases (e.g., EPA/NIH MSSS file or STIRS). The use of LRMS data in interpreting spectra of mixtures of compounds as in complex environmental samples, in addition relies on chemical ionization or low voltage electron impact ionization. These techniques minimize fragmentation and facilitate the identification of various sample components by their respective molecular ions. Particular features of the EI mass spectrum, such as the intense double ionization of polynuclear aromatic hydrocarbons, also aid in interpreting LRMS spectra of mixtures.

Samples may be introduced into the LRMS instrument via either the batch inlet or the direct insertion probe. The batch inlet is used for samples with fairly volatile components that would be lost if the solvent were evaporated. The lower limit for reliable detection of individual sample components for batch inlet spectra is on the order of 1 μg. This requires a concentration of about 500 ppm in the concentrated sample extract, since only 1-2 μL of solvent is routinely injected. The direct insertion probe is used for moderately volatile components. The absolute quantity of sample taken is between 1 ng and 1 μg, but there is no intrinsic limit on the volume of solution that can be dried onto the probe. The temperature of the direct insertion probe can be programmed to drive progressively more non-volatile species into the analyzer. At very high probe temperatures, sample decomposition can occur; this is frequently indicated by the reappearance of material with low molecular weights at probe temperatures inconsistent with their volatility.

For complex environmental samples, such as fractions from preliminary LC or HPLC separations, LRMS can indicate molecular weight ranges and probable chemical class assignments (aliphatic, aromatic, alkylphenols, etc....). Individual chemical compound identifications on the basis of LRMS may not be possible, to any high degree of certainty, for many of these complex mixtures.

2. High Resolution Mass Spectrometry

A high resolution mass spectrometer is capable of measuring masses of ions in the spectrum with an accuracy of better than 0.001 atomic mass unit. Data from the HRMS analysis are reported to four decimal places in m/e. The high accuracy and precision makes it possible to take advantage of the mass defect characteristic of atoms and use their exact masses to compute elemental composition assignments for the observed ions. The theoretical mass can be calculated for all plausible* combinations of elements corresponding to a given mass. The theoretical and measured masses are then compared and a "match" is identified when they agree to within a specified value, typically 0.002 or 0.003 amu.

In the simple case where HRMS is being used to confirm or deny the presence of a particular sample component, such as benzopyrene, it is sufficient to calculate the exact theoretical mass expected for $C_{20}H_{12}$ and see if there is a measured m/e value in the sample spectrum within 0.002 or 0.003 amu of the calculated value. This type of static peak matching to preset values (equivalent to the selected ion monitoring mode of LRMS) has a realistic detection limit on the order of 1 ng. For dynamic peak matching or scanning of the HRMS, a limit of about 1 μg is more realistic. These detection limits are typical ones for HRMS instruments utilizing electrical detection. With photographic (photoplate) detection of ions, HRMS spectra can be recorded for samples on the order of 1 ng.

There are a number of other ways in which HRMS data may be of value in the Level 2 analysis of complex organic samples. These involve the use of computer software systems to aid in interpretation of the large quantity of data (500-2000 precisely determined masses of ions with estimated abundances) that is accumulated in an HRMS run. One approach to interpreting these data is to sort the assigned elemental compositions into classes according to heteroatom composition and degree of hydrogen unsaturation (rings plus double bonds or R + DB). An alternative approach is to compare the set of measured masses with theoretical masses calculated for a list of reference compounds. The utility of these reference compound file searching procedures is obviously dependent on maintaining a relevant and appropriately comprehensive library of listed compounds and masses. If the list were as extensive as, for example, the MSSS file of LRMS spectra, the potential usefulness of HRMS file-matching in Level 2 organic analysis would be great indeed. This approach has the advantage that data interpretation can be made identical from laboratory to laboratory, and thus results of different environmental assessments can be more readily compared.

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*Limits for determining "plausible" combinations are set by the user in each application.

HRMS methods are expected to be widely used in Level 2 analysis of non-volatile polar components separated by LC and HPLC methods.

G. Infrared Spectroscopy (IR)

Infrared spectroscopy was once the most widely used tool for identification of organic compounds. Absorption in the IR range is due to vibrational energy transitions and virtually all organic compounds (and many inorganic species) have at least one absorption band in the normal IR frequency range (4000 to 400 cm^{-1}). The fact that various functional groups absorb characteristic IR frequencies, rather independently of other portions of the molecular structure, is one of the distinctive features of IR spectroscopy.

In conventional dispersive IR spectroscopy, a monochromator is used to scan vibrational frequencies and generate a plot of absorption (or transmittance) versus frequency. Modern dispersive IR instruments, suitable for Level 2 organic analysis, utilize grating monochromators to achieve high resolution (<1.5 cm^{-1} at 3000 cm^{-1}) and high wavelength accuracy (3 cm^{-1} at 3000 cm^{-1}). Most are equipped with ordinate expansion capability and some are specifically designed for interfacing with automatic data processing systems for spectral subtraction and other data manipulations. Dispersive IR instruments are by far the most common types available. Sample size requirements for dispersive IR are on the order of 1 mg for a KBr macropellet or salt plate or about 100 μg for a KBr micropellet in an instrument equipped with a beam condenser and/or ordinate expansion capability.

Individual sample components amounting to <5-10% of the total sample are likely to remain undetected.

Fourier transform infrared systems differ from conventional dispersive infrared spectrophotometers in that conventional infrared spectroscopy uses a monochromater to generate the spectral information, whereas an interferometer is used for this purpose in Fourier transform infrared spectroscopy (FTIR). The use of an interferometer to generate spectral information in the form of an interferogram (light intensity versus time) necessitates a second difference between the types of infrared spectroscopy. This difference is that FTIR systems use a dedicated digital computer to obtain the Fourier transform of the interferogram, converting it to a conventional infrared spectrum (light intensity versus wavelength or frequency). These two differences lead to two major advantages of FTIR over conventional infrared spectroscopy.

Using an interferometer results in a substantial gain in energy or light throughput as compared to a monochromator. This gain in energy results from the fact that all wavelengths of light are examined simultaneously at an interferometer and no energy is lost (as in a dispersive instrument by examining the light one wavelength at a time). This additional energy can be used in one of several ways: (a) for faster scan speeds (as fact as 0.6 sec.), (b) for up to a 30-fold increase in signal-to-noise ratio or (c) for $10^2 - 10^3$ greater sensitivity.

The availability of a dedicated computer offers several major data handling advantages. Not only can spectra be ratioed against each other to remove absorption bands due to background materials, but the computer can be used to perform spectral arithmetic. Thus, spectra can be added or subtracted from each other and also multiplied or divided. In this way, the spectra can be adjusted in size, and unwanted components can be removed from the spectra without the necessity of chemical separation. This ability to utilize a computer is not unique to Fourier transform spectroscopy, i.e., in theory a computer could be attached to a conventional dispersive infrared spectrophotometer. However, in practice, this is rarely done, whereas all Fourier transform systems use a computer. Thus, from a practical standpoint, the use of a computer is a major advantage in FTIR systems.

Recent papers have described the identification of less-than-nanogram amounts of materials and the union of FTIR with GC (41,42). In the former, the method of sample preparation is a key element of the analysis. NaCl plates are cleaved to extremely thin sections, the samples are applied using microscopes for observation, and still with the aid of a microscope, the plates are centered in 50 or 100 μm apertures and oriented in an 8X beam condenser. The sample is then scanned until a recognizable signal can be differentiated from background. The authors claim this has been successful with subnanogram quantities, e.g., of cellulose acetate, in less than two hours. In the case of the GC/FT-IR system, the paper describes a commercial system ("Chemigram") for on-the-fly analysis of vapors separated by GC.

IR spectra, whether conventional or FT-IR, will be a major tool in the characterization of non-volatile organic species in Level 2. In the general case, when the sample is a fairly complex mixture of compounds, the IR spectrum is primarily useful as an indicator of functional groups present in the sample. It will usually not be possible to determine how these functional groups are combined into various compound classes. In those specific instances where one or only a small number of components are present (as, for example, in an HPLC fraction) it may be possible to interpret the IR spectrum in terms of compound structure. If it is possible to identify a one-to-one match between bands in the sample spectrum and those in a reference spectrum of a known material, this is convincing evidence of compound identify.

H. Nuclear Magnetic Resonance Spectroscopy (NMR)

Nuclear magnetic resonance spectroscopy (NMR) as an organic analysis technique has many similarities to IR spectroscopy in the type of information provided and in the potential applicability to Level 2. The NMR spectrum arises when nuclei with magentic dipoles, or non-zero spin number, undergo radiofrequency transitions in the presence of an external magnetic field. Common nuclei with spin number 1/2 whose NMR spectra are useful in organic analysis are: ^{1}H, ^{19}F, ^{13}C and ^{31}P. The utility of NMR in organic analysis is increased because the transition frequency (chemical shift) of a given nucleus depends not only of the magnitude of the applied external magnetic field, but also on the local magnetic field generated by adjacent nuclei.

Proton NMR has been most widely investigated for organic analysis, since most organic species have an abundance of ^{1}H nuclei. In the NMR spectra of mixtures, inferences about functional groups present in the sample may be drawn from the absence or presence and intensity of peaks in these varying shift ranges. In those special cases where only one or a few components are present in the sample (as in an HPLC fraction), the fine structure (spin-spin coupling) in the proton NMR spectrum can also aid in interpretation. For conventional, continuous wave proton NMR, milligram (5-50) quantities of sample are required. A time averaging computer can be used to reduce the lower detection limit by about a factor of ten, at the expense of a considerable increase in analysis time to 20-30 hours/sample. The use of pulsed Fourier transform (FT) NMR techniques can dramatically improve the sensitivity to a lower detection limit of about 10 μg of sample by decreasing the scan time per spectrum.

Determination of ^{13}C NMR spectra in samples with natural abundance of ^{13}C (i.e., 1.1% of total carbon) are done almost exclusively in the Fourier transform mode of operation. Because of the low natural abundance milligram quantities of sample are required for ^{13}C FT-NMR. The chemical shift range of ^{13}C is about thirty times greater than that of ^{1}H, so considerably greater resolution is possible in ^{13}C NMR spectra.

It is anticipated that NMR spectroscopy will be a valuable tool in characterizing materials that are not sufficiently volatile for GC analysis or mass spectroscopy in Level 2. In many cases, sample size limitations may restrict the use of NMR to proton Fourier transform methods. In other cases, however, there may be sufficient sample to also acquire ^{13}C FT-NMR spectra. The combination of ^{1}H and ^{13}C spectra combined with IR data will probably provide the best method of characterizing high molecular weight, non-volatile species in Level 2 organic analysis.

I. Ultraviolet-Visible (UV-Vis) and Luminescence Spectroscopy (LS)

a. Ultraviolet-Visible Spectroscopy

Ultraviolet-Visible (UV-VIS) Spectroscopy is the measurement of molecular absorption of light of various wavelengths in the spectral region extending from the ultraviolet through the visible by a substance. The spectra usually are plots of the wavelength of frequency or absorption versus absorption intensities, but they may also be presented as plots of wavelength versus molar absorption, ε, or log ε. The spectra are dependent on the electronic structure of the molecular species, specifically the electronic or binding energy. Energy absorbed produces electronic transitions within a molecule, generally from the electronic ground state that is in the zero vibration level to an excited state of multiple vibration levels. Structures in which electronic transitions can take place with the absorption of minimum energy absorb at relatively long wavelengths; structures that require high energy for electronic transitions absorb at shorter wavelengths.

Two factors tend to reduce the effectiveness of absorption spectroscopy as a qualitative tool for the identification of unknown species. Spectrometric measurements of substances in solution tend to produce boardened, and therefore rather non-specific, absorption bands as a result of the presence of both vibrational and rotational energy in the excited state. Of greater import, however, are the spectral overlaps contributed by functional groups which broaden the spectral bands even more.

The use of UV-VIS spectroscopy for qualitative identification of substances in environmental assessment will be of greatest value when the analyte is known and spectra can be compared to those of standard solutions. Adequate spectra for such identifications can generally be made at concentrations on the order of micrograms per milliliter. For quantitative measurements, when the identify of the analyte is known and interferences are absent, the technique is of proven value. Adding to that value are the extensive compilations of reference spectra including those of nearly all the known carcinogenic urban air pollutants.

b. Luminescence Spectroscopy

Luminescence Spectroscopy (LS) results from the same absorption of electromagnetic radiation as occurs in UV-Vis Spectroscopy, but measures also the intensity of radiation emitted by luminescing species in returning from the excited electronic state to the ground state. Two spectra can be obtained for any luminescing compound, the emission spectrum and the excitation spectrum (which corresponds to all or part of the absorption spectrum of the material). The sensitivity of LS is 100 to 1000 times greater than that of UV-Vis absorptiometry primarily because of the method of detecting the signal of interest. In the absorption mode, the signal at any wavelength is the difference between the intensity of the source and the intensity after passing through the analyte. In LS, the intensity of the luminescence emission is measured against an essentially zero background. Good descriptions of the instrumentation available are to be found in the textbook of Guilbault (31).

In its simplest form, LS is applied to solutions of materials in solvents that are usually non-absorbing in the region of the excitation wavelength. In the case of single luminescing components, uncorrected spectra are usually sufficient to determine the compound present; quantitative data may be generated only with dilute solutions--1 μg/L to 1 ng/L--when a calibration curve is employed. In the case of mixtures, it is often possible to determine the components by selective excitation of the luminescence of each material present. Where the complexity of mixtures prevents selective excitation, a technique first described by Lloyd (32) has been useful in gaining improved resolution. In this technique, the emission and excitation monochromators of the spectrophotomer are scanned synchronously at a fixed wavelength difference, e.g., with the excitation wavelength 25 nm less than the emission wavelength.

With very complex mixtures, as well as those of only a few compounds, LS of chromatographed fractions, especially on TLC plates, can be used to identify the compounds present, as first reported by Sawicki, *et al*. (33). Spectra can be obtained with nanogram quantities of luminescing compounds. More recently, use of sensitized fluorescence to detect trace amounts (< nanogram) of polynuclear aromatic hydrocarbons has been reported (34, 35).

J. Optical Microscopy

1. General

One of the most valuable tools available to the analytical chemist for use in environmental assessment studies is the optical microscope. The fact that its value has failed to be widely appreciated in an era dominated by more specialized instruments should not discourage any practicing chemist from obtaining at least some rudimentary data by techniques that are as simple and rapid as many of them can be. More sophisticated techniques, involving optical measurements on single crystals, using polarized light and other esoteric phenomena, may be left to the few experts in chemical microscopy to whom those methods are truly familiar, but much useful information can be obtained by even a neophyte if he will acquire a few basic skills.

Figure 1a, "Level 2 Organic Analysis Scheme," shows several points at which "microscopy" is suggested for examination of collected samples and extracts that may contain particulate solids. Figure 1b, "Organic Extracts Analysis Scheme," includes "microscopy" as one of several techniques recommended for qualitative and semi-quantitative analysis of the extracts, solutions and other liquids. In the latter instance the primary purpose of the microscopic examination is to detect, and possibly to identify, crystallizable solutes in those liquids. In the former instance, the primary purpose will be to detect and characterize, or possibly to identify, pre-existing particulate matter which may contain insoluble and/or inextractable organic matter as well as inorganic solids. These initial examinations will require only rudimentary observations and descriptions of the solid substances found in the sample. The data reported will generally be used in an auxilliary or confirmatory manner, and as a means of checking on the general reasonableness and completeness of the data produced by other techniques.

2. Apparatus

The basic equipment needed to obtain the kinds of chemical information obtainable by microscopic technique are as follows:

1) A stereobinocular microscope, equipped for both incident and transmitted illumination, and capable of magnification to at least 50X.
2) An inexpensive monocular compound microscope, equipped for transmitted illumination with magnification to 100X, and with a fixed stage, suitable for use with electrically-heated auxiliary hot stage.
3) A standard petrographic microscope (rotatable stage), equipped for illumination with incident and transmitted polarized light, and with magnification to 1000X.
4) Hot stage capable of achieving temperature to 350°C.
5) Immersion liquids with refractive index (n_D 25°) of 1.44, 1.52 and 1.66. For positive identification of various organic crystalline substances, a set of immersion fluids with n_D 25° ranging from 1.4 to about 1.7 in increments of .002 will be useful.
6) Miscellaneous small tools (probes, droppers, needles), slides, cover-slips and assorted solvents.
7) Tables of data on solubility, melting point, and optical properties of crystalline organic compounds
8) Reference samples (or photomicrographs) of commonly occurring particulate substances such as flyash from various kinds of sources, pollen particles, vegatable fibers, etc. (With experience, the analyst will acquire a personal memory-bank of color, shape and size of these kinds of particulate contaminants, and will be able to identify many of the components of environmental samples at sight. At the outset, reference samples and pictures will be essential, however, and will always be helpful in conveying this kind of information to the uninitiated (36)).

3. Procedures

Gas sampling trains such as SASS generally separate any entrained solid and/or liquid particles in cyclones and filters. Microscopic examination of the "catches" of these devices should be done initially with the low-power stereo-binocular and subsequently with the petrographic microscope, using magnifications up to about 100X. Initial examination, using a measuring reticle, will show whether the desired size fractionation produced by the cyclones is satisfactory. It will also reveal some general morphological evidence; whether the particles are generally spherical (implying either that they are liquid or that they were formed as liquids and then solidified without crystallizing when cooled), whether some portion of the particles appear to be crystalline, or metallic or vegetable fibers, and whether some fraction of the "catch" appears to be liquid. Rough estimates can be made of volume fractions of each type of particle or phase seen. (36,37)

Application of a drop of methylene chloride or other proposed extractant to the sample under examination will show what proportion can be dissolved (and therefore subsequently extracted). Water-solubles and hexane-solubles can also be estimated in this way. By allowing the extract to evaporate to dryness, and examining it for crystal formation in the process, a further check on the quantity of extractables can be made.

The residue after extaction (to remove organics) can be re-examined for evidence of non-extractable organics. For example, cellulosic fibers as well as certain organic salts may be found in the residue. The microscope offers a convenient test-point for application of other extractive solvents.

Immersion of non-extracted particles, in each of the three immersion fluids (n_D^{25} = 1.44, 1.52 and 1.66) will reveal the proportion of low-electron-density solids to those of higher electron density. Generally speaking, organic compounds without heavy-atom substitution (i.e., atoms such as S, Cl, I), and without aromaticity and with little or no conjugated unsaturation will have quite low refractive indices.(37) Inorganic solids of low average atomic weight and appreciable water-solubility will also have low refractive indices, but will exhibit different solubilities in organic solvents, all of which effects are visible microscopically.

Particulate solids obtained from filtration of liquid samples may be treated similarly to those obtained from gaseous samples, with microscopic examination, using test-solvents and refractive index liquids before and after extraction of organics. Solid samples should be examined directly, prior to extraction and again after extraction. General morphology and size distribution can be recorded to complete the qualitative and rough quantitative data obtained in this way. Quantitative estimates of proportions of identifiable particulate matter should be made by visual examination, and can be expected to be good to about one significant figure (i.e., one part in ten).

Extracts should be examined microscopically for crystalline (or other) residues remaining after evaporation of the extractant from an individual sample of about 10 μL on a microscope slide. (A single cubic crystal, 10 μm in each dimension, having specific gravity = 1.0 and therefore weighing 1 ng, is readily visible at 100X magnification and readily identifiable by optical measurements such as refractive index.) Residues that crystallize readily and completely on evaporation suggest the absence of long-chain aliphatics and of non-rigid molecular structures whose presence generally inhibits crystallization. Residues that are predominantly polycrystalline, consisting of mats of very small crystals that form quickly as the last vestiges of solvent evaporate, suggest the presence of a number of different crystallizable components. (38,39)

An important tool for the chemical microscopist in the analysis of organic compounds is the hot-stage microscope (40). Samples in which individually visible crystals as small as a few micrometers in each dimension occur can be tested to determine melting points of individual solid components in a physical mixture. The presence of volatile components can also be detected, and their condensation as liquid droplets or as sublimed crystals can be observed. Mixtures of organic and inorganic particles are often resolvable by virtue of the lower melting points of the organics. By visual estimation of the fraction of a mixed sample that changes phase, from solid to liquid and/or to vapor at elevated temperature, the analyst can provide both quantitative and qualitative data to augment and support the data obtained from other sources.

Finally, in some instances, positive qualitative identifications can occasionally be made on individual crystals which contain no more than a nanogram of material, by use of easily determinable optical properties or by fusion with a test crystal of known composition on the hot stage. Both isotropic and birefringent crystals can be identified unequivocally by refractive index matching, a process that requires only a few minutes' time and minimal observational and manipulative skill. Compound identity determinations by fusion with known substances are equally simple and rapid when performed with the polarizing microscope and the hot stage. (36)

In summary, the use of the optical microscope, even at a level that would be considered quite primitive by skilled practitioners, since it makes use of only the simplest and most easily interpreted aspects of the technique, offers the analyst an abundance of data, both qualitative and quantitative, to support, extend and confirm the information he obtains from other methods. The information provided by the microscope and its accessories will often serve to guide the analyst in the choice of the most appropriate methods for separation of mixtures and identification of components. It will serve as a check on the validity of other observations, and it can provide a quick, easy and unequivocal confirmation of the identity of most organic compounds.

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APPENDIX A

Expected Distribution of MEG Category Organic Compounds In Level 1 Sampling and Systems Procedures

Each compound in the MEG list of organic compounds (8) has been reviewed to estimate where that sample would be collected in the Level Sampling and Analysis procedure. The attached charts reflect those estimates based on the information currently available. The revised Level 1 procedure has been used as the basis for the review. The estimates for many of the compounds are somewhat speculative, having been derived by analogy to known compounds, rather than being based upon actual experimental data.

Some additional data, such as molecular weight (MW), elemental composition (COMP) and boiling point (BP) were included to assist in studies of these compounds. The health effects-related MATE values for air and water were also included where available.

A compound was defined as a gas to be analized with the field GC if the boiling point was less than 100°C. Volatile compounds analyzed by the TCO procedure are those which have boiling points in the range of 100 to 300°C. The non-volatile materials analized by the GRAV procedure are those with boiling points greater than 300°C.

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Category 1

Aliphatic Hydrocarbons	MATE Air¹	MATE Water	MW²	BP °C	COMP	Air Gas	Air SASS	Field GC SGC	GC Range 1	2	3	4	5	6	TCO³	GRAV⁴	LC Fraction 1	2	3	4	5	6	7	8	Comments
A. Alkanes and Cyclic Alkanes																									
Methane	3.3E5	4.9E7	16	−161	CH_4	●			●																
Ethane	6.1E6	9.2E7	30	−89	C_2H_6	●				●															
Propane	9.0E6	1.4E8	44	−42	C_3H_8	●					●														
Butanes	1.4E6	2.1E7	58	0	C_4H_{10}	●						●													
Pentanes	1.8E6	2.7E7	72	25±	C_5H_{12}	●							●												
Cyclopentanes			70	50	C_5H_{10}	●							●												
Hexanes	3.6E5	5.4E6	86	60±	C_6H_{14}	●								●											
Cyclohexanes	1.1E6	1.6E7	84	81	C_6H_{12}	●								●											
Heptanes	1.6E6	2.4E7	100	90±	C_7H_{16}	●									●		●								
Octanes	1.5E6	2.2E7	114	110±	C_8H_{18}		●								●		●								
Nonanes	1.1E6	1.6E7	128	150±	C_9H_{20}		●								●		●								
Alkanes (C > 9)				170+	C >9		●								●		●								
B. Alkenes, Cyclic Alkenes and Dienes																									
Ethylene	5.7E6	8.6E7	28	−104	C_2H_4	●			●																
Propylene	8.6E6	1.3E8	42	−47	C_3H_6	●				●															
Butylenes			56	−5±	C_4H_8	●					●														
Butadienes	2.2E6	3.3E7	54	−5	C_4H_6	●					●														
Pentenes			70	37	C_5H_{10}	●							●												
Cyclopentadienes	2.0E5	3.0E6	66	40	C_5H_6	●							●												
Hexenes			84	68	C_6H_{12}	●								●											
Cyclohexene	1.0E6	1.5E7	82	83	C_6H_{10}	●								●											
Cyclohexadiene			80	80	C_6H_8	●								●											
Heptenes			98	95±	C_7H_{14}	●								●	●		●								
C. Alkynes																									
Acetylene	5.3E6	8.0E7	26	−84	C_2H_2	●			●																
Propyne	1.7E6	2.5E7	40	−23	C_3H_4	●				●															
Butyne			54	−8	C_4H_6	●				●															

1 Health effects basis (µg/m³) 2 Mono-isotopic, lightest isotope of each atom 3 TCO BP 100-300°C 4 GRAV BP >300°C

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Category 2

Alkyl Halides

	MATE		MW²	BP	COMP	Air		Field GC SGC	GC Range						TCO³	GRAV⁴	LC Fraction								Comments
	Air¹	Water		°C		Gas	SASS		1	2	3	4	5	6			1	2	3	4	5	6	7	8	
A. Saturated Alkyl Halides																									
Methyl bromide	6.0E4	9.0E5	94	3	CH_3Br	●						●													
Methyl chloride	2.1E5	3.2E6	50	−24	CH_3Cl	●					●														
Methyl iodide	8.5E2	1.3E4	142	42	CH_3I	●							●												
Dichloromethane (methylene	2.6E5	3.9E6	84	40	CH_2Cl_2	●							●												
chloride)						●																			
Bromodichloromethane			162	89	$CHCl_2Br$	●								●											
Dibromochloromethane			206	118	$CHClBr_2$		●								●			●							
Tribromomethane (bromo-	5.0E3	7.5E4	250	150	$CHBr_3$		●								●			●							
form)																									
Dibromodichloromethane			240	135	CCl_2Br_2		●								●			●							
Dichlorodifluoromethane	5.0E6	7.4E7	120	−30	CCl_2F_2	●					●														
Trichlorofluoromethane	5.6E6	8.4E7	136	25	CCl_3F	●						●													
Carbon tetrachloride	6.0E4	9.0E5	152	77	CCl_4	●								●											
1,2-dichloroethane	2.0E5	3.0E6	98	84	$C_2H_4Cl_2$	●								●											
(ethylene chloride)																									
1,1,1,-trichloroethane	4.5E4	6.8E5	132	74	$C_2H_3Cl_3$	●								●											
(methyl chloroform)																									
1,2-dichloro-1,2-difluoro	5.0E6	7.4E7	134	–	$C_2H_2Cl_2F_2$	●							●												
ethane																									
Hexachloroethane	1.0E4	1.5E5	234	186	C_2Cl_6		●								●			●							
Dichloropropanes	3.5E5	5.3E6	112	90±	$C_3H_6Cl_2$	●								●											
Bromobutanes			136	100±	C_4H_9Br	●								●	●			●							
Hexachlorocyclohexane	5.0E2	7.5E3	288	–	C_6Cl_6		●									●		●							
(lindane)																									
1-chlorooctane			148	182	$C_8H_{17}Cl$		●								●			●							
B. Unsaturated Alkyl Halides																									
Chloroethene (vinyl	2.6E3	3.8E4	62	−13	C_2H_3Cl	●					●														
chloride)																									
1,2-dichloroethene	7.0E5	1.1E7	96	60	$C_2H_2Cl_2$	●							●												
1,1-dichloroethene	2.6E5	3.9E6	96	37	$C_2H_2Cl_2$	●							●												
Tetrachloroethene (per-	6.7E5	1.0E7	164	121	C_2Cl_4		●								●			●							
(chloroethylene)																									
Dichloropropenes	1.1E4	1.7E5	110	80±	$C_3H_4Cl_2$	●								●											
Hexachlorobutadiene	4.1E3	6.1E4	258	215	C_4Cl_6		●								●			●							
Hexachlorocyclopenta-	1.1E2	1.7E3	270	240	C_5Cl_6		●								●			●							
diene																									

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1 Health effects basis (µg/m³) 2 Monoisotopic: lightest isotope of each atom 3 TCO BP 100-300°C 4 GRAV BP >300°C

Category 3

Ethers

	MATE		MW²	BP	COMP	Air		SGC	GC Range						TCO³	GRAV⁴	LC Fraction								Comments
	Air¹	Water		°C		Gas	SASS		1	2	3	4	5	6			1	2	3	4	5	6	7	8	
2,2'-Oxy bis propane	1.1E6	1.6E7	102	90	$C_6H_{14}O$	●						–	●	–											
2-Ethyl-4-methyl-1,3-Dioxolanes	2.3E4	3.4E5	116	118	$C_6H_{12}O$		●								●						●				
1,3-Dioxane	1.8E5	2.7E6	88	105	C_4H_8O		●								●						●				
1,4-Dioxane	1.8E5	2.7E6	88	101	C_4H_8O		●								●						●				
2-Methoxy biphenyl			184	274	$C_{13}H_{12}O$		●								●					●					

Field GC

1 Health effects basis ($\mu g/m^3$) 2 Monoisotopic, lightest isotope of each atom 3 TCO BP 100 - 300°C 4 GRAV BP > 300°C

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Category 4

Halogenated Ethers	MATE		MW²	BP	COMP	Air		Field GC							TCO³	GRAV⁴	LC Fraction								Comments
	Air¹	Water		°C		Gas	SASS	SGC	GC Ramp 1	2	3	4	5	6			1	2	3	4	5	6	7	8	
Chloromethyl methyl ether	3.7E4	5.5E5	80	56	C_2H_5OCl	●							●												
1,1'-Dichloromethyl ether			114	105	$C_2H_4OCl_2$		●								●					●					
2-Chloro-1,3-epoxypropane			92	Solid	C_3H_5OCl		●									●				●					
2-Chloroethylmethyl ether			94	92	C_3H_7OCl	●								●											
1-Chloro-1,3-oxetane			92	—	C_3H_5OCl		●									●				●					
Chloromethylethyl ether			94	80	C_3H_7OCl	●								●											
Chloro ethyl ethyl ether			108	100±	C_4H_9OCl		●								●					●					
1,1'-Dichlorodiethyl ether	3.0E4	4.5E5	142	116	$C_4H_8OCl_2$		●								●					●					
1,2-Dichlorodiethyl ether			142	140	$C_4H_8OCl_2$		●								●					●					
1,2-Dichloroethyl ethyl ether			142	145	$C_4H_8OCl_2$		●								●					●					
2,2'-Dichlorodiethyl ether	3.0E4	4.5E5	142	178	$C_4H_8OCl_2$		●								●					●					
a-Chlorobutylethyl ether			136	—	$C_6H_{13}OCl$		●									●				●					
bis-(1-chloroisopropyl)ether			170	—	$C_6H_{12}OCl_2$		●									●				●					
1,2-Dichlorodiisobutyl ether			190	—	$C_8H_{16}OCl_2$		●									●				●					
Bromophenyl phenyl ether			248	310	$C_{12}H_9OBr$		●									●				●					

1 Health effects basis (µg/m³) 2 Monoisotopic: lightest isotope of each atom 3 TCO BP 100 300°C 4 GRAV BP 300°C

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Category 5

Alcohols	MATE		MW[2]	BP	COMP	An		Field GC SGC	GC Range						TCO[3]	GRAV[4]	LC Fraction								Comments
	Air[1]	Water		°C		Gas	SANS		1	2	3	4	5	6			1	2	3	4	5	6	7	8	
A. Primary Alcohols																									
Methyl alcohol	2.6E5	3.9E6	32	64	CH_3OH	●								●											
Ethyl alcohol	1.9E6	2.9E7	46	78	C_2H_5OH	●								●											
1-propanol	5.0E5	7.5E6	60	97	C_3H_7OH	●								●											
1-butanol	1.5E5	2.3E6	74	118	C_4H_9OH		●								●							●			
1-pentanol	3.6E5	5.4E6	88	138	$C_5H_{11}OH$		●								●							●			
B. Secondary Alcohols																									
2-propanol	9.8E5	1.5E7	60	82	C_3H_7OH	●								●											
2-butanol	4.5E5	6.8E6	74	99	C_4H_9OH	●								●											
2-pentanol; 3-pentanol	3.6E5	5.4E6	88	120	$C_5H_{11}OH$		●								●							●			
α-hydroxytoluene	5.5E4	8.3E5	108	205	C_7H_7OH		●								●							●			
2,6-dimethyl-4-heptanol	1.6E5	2.4E6	144	178	$C_9H_{19}OH$		●								●							●			
Borneol	9.0E4	1.4E6	154	212	$C_{10}H_{17}OH$		●								●							●			
C. Tertiary Alcohols																									
2-methyl propanol (tert-butyl alcohol)	3.0E5	4.5E6	74	82	C_4H_9OH	●								●											
α-methyl-αhydroxytoluene	1.8E4	2.7E5	122	—	C_8H_9OH		●									●						●			
α-terpineol	1.9E5	2.9E6	154	220	$C_{10}H_{17}OH$		●								●							●			
Isoborneol			154	SOLID	$C_{10}H_{17}OH$		●									●						●			

1 Health effects basis (µg/m³) 2 Monoisotopic, lightest isotope of each atom. 3 TCO BP 100-300°C 4 GRAV BP >300°C

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Category 6

	MATE		MW²	BP	COMP	Air		Field GC							TCO³	GRAV⁴	LC Fraction								Comments
								SGC	GC Range																
	Air¹	Water		°C		Gas	SASS		1	2	3	4	5	6			1	2	3	4	5	6	7	8	
Glycols, Epoxides																									
A. Glycols																									
Ethylene glycol (1,2-Ethanediol)	1.0E4	1.5E5	62	198	$C_2H_6O_2$		●								●							●			
Propylene glycol (1,2-Propanediol)	3.6E5	5.4E6	76	188	$C_3H_8O_2$		●								●							●			
B. Epoxides																									
2,3-epoxy-1 propanol	1.5E5	2.3E6	74	166	$C_3H_6O_2$		●								●							●			
1-chloro-2,3-epoxy propane (α-Epichlorohydrin)	1.6E4	2.4E5	92	116	C_3H_5ClO		●								●							●			

1 Health effects basis (μg/m³) 2 Monoisotopic, lightest isotope of each atom 3 TCO BP 100 300°C 4 GRAV BP > 300°C

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Category 7

Aldehydes, Ketones

	MATE		MW²	BP	COMP	Air		Field GC	GC Range						TCO³	GRAV⁴	LC Fraction								Comments
	Air¹	Water		°C		Gas	SASS	SGI	1	2	3	4	5	6			1	2	3	4	5	6	7	8	
A. Aldehydes*																									
Formaldehyde	1.6E3	2.4E4	30	−21	CH_2O	●					●														
Acetaldehyde	1.8E5	2.7E6	44	20	C_2H_4O	●						●													
Propionaldehyde	3.6E4	5.4E5	58	50	C_3H_6O	●							●												
Acrolein	2.5E2	3.8E3	56	52	C_3H_4O	●							●												
Butyraldehyde	1.1E5	1.7E6	72	75	C_4H_8O	●								●											
Bromoform butanal			306	—	$C_4H_5OBr_3$		●									●				●					
3-Methylbutanal	3.9E5	5.8E6	86	92	$C_5H_{10}O$	●								●											
Benzaldehyde	5.9E4	8.8E5	106	179	C_7H_6O		●								●					●					
B. Ketones																									
Acetone	2.4E6	3.6E7	58	56	C_3H_6O	●							●												
Tetrachloroacetone			194	180	$C_3H_2OCl_4$		●								●					●					
Butanone	5.9E5	8.9E6	72	80	C_4H_8O	●								●											
Isophrone	2.5E4	3.8E5	138	215	$C_9H_{14}O$		●								●					●					
Camphor (d)	1.2E4	1.8E5	152	204	$C_{10}H_{16}O$		●								●					●					
Acetophenone	4.1E4	6.1E5	120	202	C_8H_8O		●								●					●					
Chlorohydroxy benzophenone			233	—	$C_{13}H_9O_2Cl$		●									●				●					
5,6-Benzo-9-anthrone			244	—	$C_{18}H_{12}O$		●									●				●					
Dihydro(d)carbone			152	221	$C_{10}H_{16}O$		●								●					●					

1 Health effects basis (ug/m³); Minimum acute lightest ... of each ...   3 TCO BP 100-300°C   4 GRAV BP >300°C

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Category 8

Carboxylic Acids and Derivatives	MATE		MW²	BP	COMP	Air		Field GC							TCO³	GRAV⁴	LC Fraction								Comments
	Air¹	Water		°C		Gas	SASS	SGC	GC Range 1	2	3	4	5	6			1	2	3	4	5	6	7	8	
A. Carboxylic Acids																									
Formic acid	9.0E3	1.4E5	46	100	CH_2O_2		●								●								●		
Acetic acid	2.5E4	3.8E5	60	117	$C_2H_4O_2$		●								●								●		
Maleic acid	1.0E3	1.5E4	116	138	$C_4H_4O_4$		●								●								●		
Benzoic acid	1.4E5	2.1E6	122	249	$C_7H_6O_2$		●								●								●		
Phthalic acid	6.0E3	9.0E4	166	solid	$C_8H_6O_4$		●									●							●		
Long chain acids				300-380	C_{11}-C_{18}		●									●							●		
B. Carboxylic Acids with Additional Functional Groups																									
Hydroxyacetic acid	8.8E4	1.3E6	76	solid	$C_2H_4O_3$		●									●							●		
Hydroxybenzoic acids	4.0E4	6.0E5	138	solid	$C_7H_6O_3$		●									●							●		
3-hydroxypropanoic acid lactone	3.2E2	4.8E3	72	162	$C_3H_4O_2$		●								●								●		
C. Amides																									
Formamide	3.0E4	4.5E5	45	210	CH_3NO		●								●								●		
Acetamide	4.5E5	6.8E6	59	221	C_2H_5NO		●								●								●		
6-aminohexanoic acid			131	solid	$C_6H_{13}NO_2$		●									●								●	
D. Esters																									
Methyl methacrylate	4.1E5	6.2E6	100	100	$C_5H_8O_2$		●								●							●			
Phthalates	5.0E3	7.5E4		280°			●								●							●			
Adipates	1.9E4	2.8E5		130-175			●								●							●			
Long chain esters				—																					
Methyl benzoate	1.5E5	2.6E6	136	200	$C_8H_8O_2$		●								●							●			
Phenyl benzoate			198	314	$C_{13}H_{10}O_2$		●									●						●			
Di-2-ethylhexyl phthalate			279	231	$C_{24}H_{38}O_4$		●								●							●			
6-Aminohexanoic acid (e-caprolactam)	1.0E3	1.5E4	112	solid	$C_6H_{11}NO$		●									●							●		

1 Health effects basis (µg/m³) 2 Mono-isotopic, highest isotope of each atom 3 TCO BP 100-300°C 4 GRAV BP >300°C

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Category 9

Nitriles	MATE		MW²	BP	COMP	Air		SGC	GC Range						TCO³	GRAV⁴	LC Fraction								Comments
	Air¹	Water		°C		Gas	SASS		1	2	3	4	5	6			1	2	3	4	5	6	7	8	
Acetonitrile	7.0 E4	1.1 E6	41	81	C_2H_3N	●								●											
1-Cyanoethane (acrylonitrile)	4.5E4	6.8E5	53	77	C_3H_3N	●								●											
1,4-Dicyano-1-hydroxy butane			124	>500	$C_6H_8ON_2$		●									●						●			
Benzonitrile	3.2E4	9.9E5	103	191	C_7H_5N		●								●					●					
Naphthonitriles			153	300±	$C_{11}H_7N$		●									●				●					

Field GC

1 Health effects basis (µg/m³) Mono-isotopic, lightest isotope of each atom 3 TCO BP 100 300°C 4 GRAV BP 300°C

Category 10

Amines	MATE Air[1]	MATE Water	MW[2]	BP °C	COMP	Air Gas	Air SASS	Field GC SGC	GC Range 1	GC Range 2	GC Range 3	GC Range 4	GC Range 5	GC Range 6	TCO[3]	GRAV[4]	IR Fraction 1	IR Fraction 2	IR Fraction 3	IR Fraction 4	IR Fraction 5	IR Fraction 6	IR Fraction 7	IR Fraction 8	Comments
A. Primary Amines																									
Ethylamine	1.0E4	2.7E5	45	16	C_2H_7N	●						●													
Ethanolamine	6.0E3	9.0E4	61	171	C_2H_7NO		●								●							●			
3-Aminopropene			57	58	C_3H_7N	●							●												
Propanolamine	1.3E5	1.9E6	75	160	C_3H_9NO		●								●							●			
1-Aminobutane	1.5E4	2.3E5	75	78	$C_4H_{11}N$	●								●											
2-Aminobutane	1.5E4	2.3E5	75	63	$C_4H_{11}N$	●								●											
Cyclohexylamine	4.0E4	6.0E5	99	134	$C_6H_{13}N$		●								●							●			
1,2-Diaminoethane	2.5E4	3.8E5	60	116	$C_2H_8N_2$		●								●							●			
Aniline	1.9E4	3.0E5	93	184	C_6H_7N		●								●							●			
2-Aminotoluene	1.1E2	1.7E3	107	200	C_7H_9N		●								●							●			
Dimethylaniline	2.5E4	3.8E5	121	193	$C_8H_{11}N$		●								●							●			
Anisidines	5.0E2	7.5E3	123	240±	C_7H_9NO		●								●							●			
Aminodiphenyls	1.3E3	2.0E4	169	300±	$C_{12}H_{11}N$		●									●						●			
Aminonaphthalenes	5.6E2	8.5E3	143	300+	$C_{10}H_9N$		●									●						●			
1,4-Diaminobenzene	4.5E3	6.8E4	104	267	$C_6H_8N_2$		●								●							●			
4,4'-Diaminodiphenyl	1.4E4	2.1E5	184	400	$C_{12}H_{12}N_2$		●									●						●			
3,3'-Dichlorobenzidine	6.6E3	9.9E4	224	solid	$C_{12}H_{10}Cl_2$		●									●							●		
4,4'-Methylene bis (2-chloroaniline)	2.2E2	3.3E3	266	solid	$C_{13}H_{12}N_2Cl_2$		●									●							●		
B. Secondary Amines																									
Ethyleneimine	3.3E2	5.0E3	43	57	C_2H_5N	●							●												
Dimethylamine	1.8E4	2.7E5	45	7	C_2H_7N	●							●												
Ethylmethylamine			59	/	C_3H_9N	●							●												
Diethylamine	7.5E4	1.1E6	73	56	$C_4H_{11}N$	●							●												
Morpholine	7.0E4	1.1E6	87	129	C_4H_9N		●								●							●			
C. Tertiary Amines																									
N,N-Dimethylaniline	2.5E4	3.8E5	121	194	$C_8H_{11}N$		●								●							●			

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1 Health effects basis ($\mu g/m^3$) 2 Monoisotopic - lightest isotope of each atom 3 TCO BP 100 - 300°C 4 GRAV BP > 300°C

Category 11

Field GC

Azo Compounds, Hydrazine, and Derivatives	MATE		MW[2]	BP	COMP	Air		SGC	GC Range						TCO[3]	GRAV[4]	LC Fraction								Comments
	Air[1]	Water		°C		Gas	SASS		1	2	3	4	5	6			1	2	3	4	5	6	7	8	
Diazomethane	4.0E2	6.0E3	42	−23	CH_2N_2	●					●														
Hydrazine				113	N_2H_4		●								●								●		
Dimethylhydrazines	1.0E3	1.5E4	60	60-80	$C_2H_8N_2$	●								●											
Diphenylhydrazines	1.4E4	2.0E5	184	220	$C_{12}H_{12}N_2$		●								●								●		

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1 Health effects basis (μg/m³) 2 Mono-isotopic: lightest isotope of each atom 3 TCO BP 100–300°C 4 GRAV BP > 300°C

Category 12

Nitrosamines

	MATE Air¹	MATE Water	MW²	BP °C	COMP	Air Gas	Air SASS	SGt	GC Range 1	2	3	4	5	6	TCO³	GRAV⁴	LC Fraction 1	2	3	4	5	6	7	8	Comments
Dimethylamine-N-Nitroso	1.2E0	1.8E1	74	154	$C_2H_6N_2O$		●								●						●				
Diethylamine-N-Nitroso	1.2E2	1.8E3	102	177	$C_4H_{10}N_2O$		●								●						●				
Dipropylamine-N-Nitroso	2.4E3	3.6E4	130	206	$C_6H_{14}N_2O$		●								●						●				
Diisopropylamine-N-Nitroso	3.8E4	5.8E5	130	194	$C_6H_{14}N_2O$		●								●						●				
Dipentylamine-N-Nitroso			186		$C_{10}H_{22}N_2O$		●									●					●				
Aniline, N-Methyl-N-Nitroso	1.3E3	1.9E4	136	225	$C_7H_8N_2O$		●								●						●				
Diphenylamine-N -Nitroso	7.4E4	1.1E6	198	SOLID	$C_{12}H_{10}N_2O$		●									●					●				

1 Health effects basis (µg/m³); [illegible]

3 TCO BP 100-300°C

4 GRAV BP >300°C

Category 13

Mercaptans, Sulfides and Disulfides

	MATE		MW[2]	BP	COMP	Air		Field GC	GC Ramp						TCO[3]	GRAV[4]	LC Fraction								Comments
	Air[1]	Water		°C		Gas	SASS	SGC	1	2	3	4	5	6			1	2	3	4	5	6	7	8	
A. Mercaptans																									
Methyl mercaptan	1.0E3	1.5E4	48	6	CH_3SH	●		●																	
Ethyl mercaptan	1.0E3	1.5E4	62	35	C_2H_5SH	●		●																	
Propyl mercaptans	8.1E4	1.2E6	76	60±	C_3H_7SH	●		●																	
Butyl mercaptans	1.5E3	2.3E4	90	80±	C_4H_9SH	●		●																	
Benzenethiol	2.1E3	3.1E4	110	168	C_6H_5SH		●								●							●			
1-anthrathiol			210	—	$C_{14}H_9SH$		●									●						●			
Perchloromethyl mercaptan	8.0E2	1.2E4	150	149	CCl_3SH		●								●							●			
B. Sulfides, Disulfides																									
Dimethyl sulfide	2.4E4	3.6E5	62	37	C_2H_6S	●		●																	
Diethyl sulfide			90	92	$C_4H_{10}S$	●		●																	
Phenyl sulfide	9.6E4	1.4E6	186	296	$C_{12}H_{10}S$		●								●							●			
Methyl disulfide			94	116	$C_2H_6S_2$		●								●							●			

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[1] Health effects basis (µg/m³)

[2] Monoisotopic, lightest isotope of each atom

[3] TCO BP 100–300°C

[4] GRAV BP > 300°C

Category 14

Sulfonic Acids, Sulfoxides	MATE		MW²	BP	COMP	Air		Field GC SGC	GC Range						TCO³	GRAV⁴	LC Fraction								Comments
	Air¹	Water		°C		Gas	SASS		1	2	3	4	5	6			1	2	3	4	5	6	7	8	
A. Sulfonic Acids																									
Benzenesulfonic acid	4.0E4	6.0E5	158	solid	$C_6H_6SO_3$		●									●								●	
9,10-Anthraquinone-disulfonic acids			368	solid	$C_{14}H_6O_2-(SO_3H)_2$		●									●								●	
B. Sulfoxides																									
Dimethyl sulfoxide	8.1E2	1.2E3	78	189	C_2H_6SO		●								●									●	

1 Health effects basis (µg/m³) 2 Monoisotopic: lightest isotope of each atom 3 TCO BP 100-300°C 4 GRAV BP >300°C

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Category 15

Benzene, Substituted Benzene

Hydrocarbons

	MATE		MW^2	BP	COMP	Rx		Field GC																
								SGC	GC Range						TCO^3	GRAV^4	LC Fraction								Comments
	Air^1	Water		°C		Gas	SASS		1	2	3	4	5	6			1	2	3	4	5	6	7	8	
Benzene	3.0E3	4.5E4	78	80	C_6H_6	●								●											
Toluene	3.8E5	5.6E6	92	110	C_7H_8		●								●			●							
Ethyl benzene	4.4E5	6.5E6	106	136	C_8H_{10}		●								●			●							
Styrene	4.2E5	6.3E6	104	145	C_8H_8		●								●			●							
Propyl benzene	2.2E5	3.3E6	120	159	C_9H_{12}		●								●			●							
Isopropyl benzene	6.3E4	9.5E5	120	152	C_9H_{12}		●								●			●							
Butyl benzene	2.3E5	3.4E6	134	183	$C_{10}H_{14}$		●								●			●							
Biphenyls	1.0E3	1.5E4	154	255	$C_{12}H_{10}$		●								●			●							
4,4'-diphenylbiphenyl			306	428	$C_{24}H_{18}$		●									●		●							
Xylenes	4.4E5	6.5E6	106	140±	C_8H_{10}		●								●			●							
Dialkyl benzenes	2.3E5	3.4E6		/			●									●		●							
Tetrahydronaphthalene	1.3E5	2.0E6	132	207	$C_{10}H_{12}$		●								●			●							
Dihydronaphthalene	1.3E5	2.0E6	130	/	$C_{10}H_{10}$		●									●		●							
Terphenyls	9.0E3	1.4E5	230	350±	$C_{18}H_{14}$		●									●			●						
Trimethyl benzenes	1.2E5	1.8E6	120	170±	C_9H_{12}		●								●			●							
Tetramethyl benzenes			134	200±	$C_{10}H_{14}$		●								●			●							

1 Health effects basis (ug/m³) 2 Monoisotopic, lightest isotope of each atom   3 TCO BP 100 300°C   4 GRAV BP > 300°C

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Category 16

	MATE		MW²	BP	COMP	Air		Field GC							TCO³	GRAV⁴	LC Fraction								Comments
								SGC	GC Range																
Halogenated Aromatic Compounds	Air¹	Water		°C		Gas	SASS		1	2	3	4	5	6			1	2	3	4	5	6	7	8	
A. Ring Substituted Aromatics																									
Chlorobenzene	3.5E5	5.3E6	112	131	C_6H_5Cl		●								●			●							
Bromo and dibromobenzenes			156/234	150/220	$C_6H_5Br(2)$		●								●			●							
Bromochlorobenzenes			190	200±	C_6H_4BrCl		●								●			●							
1,2-dichlorobenzene	3.0E5	4.5E6	146	179	$C_6H_4Cl_2$		●								●			●							
1,3-dichlorobenzene			146	172	$C_6H_4Cl_2$		●								●			●							
1,4-dichlorobenzene	4.5E5	6.8E6	146	174	$C_6H_4Cl_2$		●								●			●							
Polychlorinated benzenes	3.4E4	5.1E5	282	HIGH	C_6Cl_6		●								●				●						
Chloronaphthalenes	6.9E4	1.0E6	162	250+	$C_{10}H_7Cl$		●								●				●						
Polychlorinated biphenyls	5.0E2	7.5E3		270+			●								●				●						
B. Aromatics with Halogenated Alkyl Side Chain																									
α-chlorotoluene	5.0E3	7.5E4	126	180	C_7H_7Cl		●								●			●							
bis-(chloromethyl)-benzene			174	240±	$C_8H_8Cl_2$		●								●			●							

1 Health effects basis (µg/m³) 2 Monoisotopic, lightest isotope of each atom 3 TCO BP 100–300°C 4 GRAV BP > 300°C

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Category 17

Aromatic Nitro Compounds

	MATE		MW²	BP	COMP	Air		Field GC							TCO³	GRAV⁴	LC Fraction								Comments
	Air¹	Water		°C		Gas	SASS	SGC	GC Range 1	2	3	4	5	6			1	2	3	4	5	6	7	8	
Nitrobenzene	5.0E3	7.5E4	123	210	$C_6H_5NO_2$		●								●					●					
4-nitrobiphenyl; nitrobi-	1.3E3	2.0E4	199;199	200 –	$C_{12}H_9NO_2$		●								●					●					
phenyls				340			●								●	●				●					
Chloronitrobenzenes	1.6E4	2.5E4	157	240±	$C_6H_4ClNO_2$		●								●					●					
Methoxynitrobenzenes	4.5E3	6.8E4	153	260±	$C_7H_7NO_3$		●								●						●				
Dinitrotoluenes	1.5E3	2.3E4	182	300±	$C_7H_6(NO_2)_2$		●									●					●				

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1 Health effects basis (µg/m³) 2 Monoisotopic: lightest isotope of each atom   3 TCO BP 100-300°C   4 GRAV BP >300°C

Category 18

Phenols	MATE		MW²	BP	COMP	Air		SGC	GC Range						TCO³	GRAV⁴	LC Fraction								Comments
	Air¹	Water		°C		Gas	SASS		1	2	3	4	5	6			1	2	3	4	5	6	7	8	
A. Monohydrics																									
Phenol	1.9E4	5.0E0	94	182	C_6H_6O		●								●							●			
Methyl phenols (cresols)	2.2E4	5.0E0	108	200±	C_7H_8O		●								●							●			
2-methoxyl phenol	3.3E4	5.0E0	124	205	$C_7H_8O_2$		●								●							●			
Ethylphenols			122	210±	$C_8H_{10}O$		●								●							●			
Hydroxybiphenyls	2.3E4	5.0E0	170	280+	$C_{12}H_{10}O$		●								●							●			
2,2'-dihydroxydiphenyls	6.8E3	5.0E0	186	SOLID	$C_{12}H_{10}O_2$		●									●						●			
Dimethylphenols (Xylenols)	1.3E4	5.0E0	122	220±	$C_8H_{10}O$		●								●							●			
Polyalkylphenols	1.5E4	5.0E0		HIGH			●									●						●			
B. Dihydrics, Polyhydrics																									
1,2-dihydroxybenzene	2.0E4	5.0E0	110	245	$C_6H_6O_2$		●								●							●			
1,3-dihydroxybenzene	4.5E4	5.0E0	110	178	$C_6H_6O_2$		●								●							●			
1,4-dihydroxybenzene	2.0E3	5.0E0	110	285	$C_6H_6O_2$		●								●							●			
1,2,3-trihydroxybenzenes	3.6E4	5.0E0	126	309	$C_6H_6O_3$		●									●						●			
C. Fused ring hydroxy compounds																									
α-naphthanol	1.2E5	5.0E0	144	278	$C_{10}H_8O$		●								●							●			
β-naphthanol	1.1E5	5.0E0	144	285	$C_{10}H_8O$		●								●							●			
Phenthrols		5.0E0		SOLID			●									●						●			
Indanols	1.5E5	5.0E0	134	235	$C_9H_{10}O$		●								●							●			
Acenaphthenols		5.0E0	170	SOLID	$C_{12}H_{10}O$		●									●						●			
2-hydroxyfluorene		5.0E0	182	SOLID	$C_{13}H_{10}O$		●									●						●			
2-hydroxydibenzofuran		5.0E0	184	SOLID	$C_{12}H_8O$		●									●						●			

Field GC

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1 Health effects basis (μg/m³) 2 Mono-isotopic, lightest isotope of each atom 3 TCO BP 100-300°C 4 GRAV BP > 300°C

Category 19

Field GC

Halophenols	MATE		MW²	BP	COMP	Air		SGC	GC Range						TCO³	GRAV⁴	LC Fraction								Comments
	Air¹	Water		°C		Gas	SASS		1	2	3	4	5	6			1	2	3	4	5	6	7	8	
2-chlorophenol	3.0E4	5.0E0	128	175	C_6H_5OCl		●								●							●			
2,4-dichlorophenol	7.0E3	5.0E0	162	210	$C_6H_4OCl_2$		●								●							●			
Pentachlorophenol	5.0E2	5.0E0	264	310	C_6HOCl_5		●									●							●		
Chlorinated cresols	2.3E4	5.0E0	125	190⁺	C_7H_7OCl		●								●							●			

1 Health effects based (µg/m³) 2 Monoisotopic lightest isotope of each atom 3 TCO BP 100 – 300°C 4 GRAV BP > 300°C

2-27-78

Category 20

Nitrophenols	MATE Air[1]	MATE Water	MW[2]	BP °C	COMP	Air Gas	Air SASS	Field GC SGC	GC Range 1	GC Range 2	GC Range 3	GC Range 4	GC Range 5	GC Range 6	TCO[3]	GRAV[4]	LC Fraction 1	LC Fraction 2	LC Fraction 3	LC Fraction 4	LC Fraction 5	LC Fraction 6	LC Fraction 7	LC Fraction 8	Comments
2-nitrophenol	5.8E4	5.0E0	139	216	$C_6H_5NO_3$		●								●								●		
3-nitrophenol	2.0E4	5.0E0	139	194	$C_6H_5NO_3$		●								●								●		
4-nitrophenol	1.6E4	5.0E0	139	279	$C_6H_5NO_3$		●								●								●		
Dinitrophenols	1.4E3	5.0E0	184	solid	$C_6H_4N_2O_5$		●									●							●		
o-cresol, dinitro	2.0E2	5.0E0	198	solid	$C_7H_6N_2O_5$		●									●							●		
p-cresol, dinitro	6.8E2	5.0E0	198	solid	$C_7H_6N_2O_5$		●									●							●		
2-amino-4,6-dinitrophenol	4.6E4	5.0E0	198	solid	$C_6H_5N_3O_5$		●									●							●		
Trinitrophenol	1.0E2	5.0E0	229	solid	$C_6H_3N_3O_7$		●									●							●		

2-23-78

1 Health effects basis (μg/m³) 2 Monoisotopic: lightest isotope of each atom 3 TCO BP 100 - 300°C 4 GRAV BP > 300°C

Category 21

Fused Polycyclic Hydrocarbons	MATE		MW²	BP	COMP	Air		SGC	GC Range						TCO³	GRAV⁴	LC Fraction								Comments
	Air¹	Water		°C		Gas	SASS		1	2	3	4	5	6			1	2	3	4	5	6	7	8	
Naphthalene	5.0E4	7.5E5	128	218	$C_{10}H_8$		●								●			●							
Monoalkyl naphthalenes	2.3E5	3.4E6		240⁺			●								●			●							
Phenyl naphthalenes			204	340	$C_{16}H_{12}$		●									●			●						
Dimethyl naphthalenes	2.3E5	3.4E6	156	260⁺	$C_{12}H_{12}$		●								●			●							
Acenaphthene; acenaphthylene			154;152	270±	$C_{12}H_{10}$; $C_{12}H_8$		●								●				●						
Anthracene	5.6E4	8.4E5	178	340	$C_{14}H_{10}$		●									●			●						
2,7-dimethylanthracene			206	370	$C_{16}H_{14}$		●									●			●						
Phenanthrene	1.6E3	2.4E4	178	340	$C_{14}H_{10}$		●									●			●						
Methylphenanthrenes	3.0E4	4.6E5	192	350±	$C_{15}H_{12}$		●									●			●						
Naphthacene			228	—	$C_{18}H_{12}$		●									●			●						
1,2-benzanthracene	4.5E1	6.7E2	228	435	$C_{18}H_{12}$		●									●			●						
9,10-dimethyl-1,2-benzanthracene	2.6E-1	3.9E0	256	—	$C_{20}H_{16}$		●									●			●						
Benzo(c)phenanthrene	2.7E4	4.1E5	228	—	$C_{18}H_{12}$		●									●			●						
Chrysene	2.2E3	3.3E4	228	448	$C_{18}H_{12}$		●									●			●						
Methylchrysenes	1.8E3	2.7E4	242	—	$C_{19}H_{14}$		●									●			●						
Triphenylene			228	438	$C_{18}H_{12}$		●									●			●						
Pyrene	2.3E5	3.5E6	202	393	$C_{16}H_{10}$		●								●				●						
1-methyl pyrene			216	410	$C_{17}H_{12}$		●									●			●						
1,2-benzonaphthacene			278	~500	$C_{22}H_{14}$		●									●			●						
Benzo(b)chrysene	1.6E4	2.4E5	278	~500	$C_{22}H_{14}$		●									●			●						
1,2:3,4-dibenzanthracene	9.9E3	1.5E5	278	—	$C_{22}H_{14}$		●									●			●						
1,2:5,6-dibenzanthracene	9.3E-2	1.4E0	278	—	$C_{22}H_{14}$		●									●			●						
Benzo[a]pyrene	2.0E-2	3.0E-1	256	496	$C_{20}H_{12}$		●									●			●						
Benzo[e]pyrene	3.0E3	4.6E4	256	493	$C_{20}H_{12}$		●									●			●						
Perylene			256	—	$C_{20}H_{12}$		●									●			●						
Picene (dibenzo(a,i)phenanthrene)	2.5E3	3.8E4	278	520	$C_{22}H_{14}$		●									●			●						
Dibenzo[a,h]pyrene	3.7E3	5.6E4	302	—	$C_{24}H_{14}$		●									●			●						
Dibenzo[a,i]pyrene	4.3E1	6.5E2	302	—	$C_{24}H_{14}$		●									●			●						
Dibenzo[a,l]pyrene	1.1E3	1.6E4	302	—	$C_{24}H_{14}$		●									●			●						
Benzo[g,h,i]perylene			277	500	$C_{22}H_{12}$		●									●			●						
Coronene			300	525	$C_{24}H_{12}$		●									●			●						

Field GC

1 Health effects basis ($\mu g/m^3$) 2 Monoisotopic, lightest isotope of each atom 3 TCO BP 100-300°C 4 GRAV BP >300°C

2-27-78

Category 22

Fused Non-Alternant Polycyclic Hydrocarbons

	MATE		MW²	BP	COMP	Air		Sol.	GC Ramp						TCO³	GRAV⁴	LC Fraction								Comments
	Air¹	Water		°C		Gas	SASS		1	2	3	4	5	6			1	2	3	4	5	6	7	8	
Indene and derivatives	4.5E4	6.8E5	116	182*	C_9H_8		●								●			●							
Dicyclopentadiene	1.6E4	2.4E5	132	170	$C_{10}H_{12}$		●								●			●							
Fluorene and derivatives			166	298*	$C_{13}H_{10}$		●								●			●							
Cyclopentanonaphthalene			182	299	$C_{13}H_{10}O$		●								●			●							
2,3-benzofluorene			216	402	$C_{17}H_{12}$		●									●			●						
Fluoranthene; tetrahydrofluoranthene	9.0E4	1.4E6	202; 206	382; 365	$C_{16}H_{10}$; $C_{16}H_{14}$		● ●									● ●			● ●						
1,2-benzofluorene			216	413	$C_{17}H_{12}$		●									●			●						
4-H-cyclopenta(def)phenanthrene			190	353	$C_{15}H_{10}$		●									●			●						
Benzo(k)fluoranthene	1.6E3	2.5E4	252	480	$C_{20}H_{12}$		●									●			●						
Benzo(e)fluoranthene	9.0E2	1.4E4	252	—	$C_{20}H_{12}$		●									●			●						
Benzo(j)fluoranthene	6.5E3	9.8E4	252	480	$C_{20}H_{12}$		●									●			●						
1,2:5,6-dibenzofluorene	1.3E4	2.0E5	266	—	$C_{21}H_{14}$		●									●			●						
3-methyl cholanthrene	3.8E0	5.6E1	268	~300	$C_{21}H_{16}$		●									●			●						
Indeno (1,2,3,c,d)pyrene	1.6E3	2.4E4	276	solid	$C_{22}H_{12}$		●									●			●						
Truxene (tribenzylene benzene)			340	365	$C_{27}H_{18}$		●									●			●						

1 Health effects base (µg/m³) 2 [illegible] highest isotope of each atom 3 TCO BP 100-300°C 4 GRAV BP >300°C

2-27-78

Category 23

Heterocyclic Nitrogen Compounds	MATE		MW[2]	BP	COMP	Air		Field GC							TCO[3]	GRAV[4]	LC Fraction								Comments
								SGC	GC Range																
	Air[1]	Water		°C		Gas	SASS		1	2	3	4	5	6			1	2	3	4	5	6	7	8	
A. Pyridine and Substituted																									
Pyridines																									
Pyridine	1.5E4	2.3E5	79	116	C_5H_5N		●								●				●						
Monosubstituted alkyl pyridines				150$^+$			●								●				●						
phenyl pyridines			162	270$^+$	$C_{11}H_9N$		●								●				●						
Chloropyridine	4.8E3	7.2E4	113	150$^\pm$	C_5H_4NCl		●								●				●						
Disubstituted, polysubstituted pyridines	2.7E4	4.1E5		160$^\pm$			●								●				●						
B. Fused 6-membered Ring Heterocycles																									
Quinoline, isoquinoline	1.6E4	2.4E5	129	240$^\pm$	C_9H_7N		●								●							●			
Methylquinolines, methylisoquinolines	1.5E4	8.3E5	143	250$^\pm$	$C_{10}H_9N$		●								●							●			
Dimethylquinolines, dimethylisoquinolines			157	270$^\pm$	$C_{11}H_{11}N$		●								●							●			
Acridine	9.0E4	1.4E6	179	346	$C_{13}H_9N$		●									●						●			
Dihydroacridine			181	300	$C_{13}H_{11}N$		●									●						●			
Benzo(c)quinoline			179	350	$C_{13}H_9N$		●									●						●			
Benzo(f)quinoline			181	350	$C_{13}H_{11}N$		●									●						●			
Benzo(h)quinoline			179	338	$C_{13}H_9N$		●									●						●			
Benz(a)acridine			229	438	$C_{17}H_{11}N$		●									●						●			
Benz(c)acridine	1.1E4	1.6E5	229	438	$C_{17}H_{11}N$		●									●						●			
Dibenz(a,j)acridine	2.5E2	3.7E3	258	–	$C_{21}H_{13}N$		●									●						●			
Dibenz(a,h)acridine	2.2E2	3.4E3	258	–	$C_{21}H_{13}N$		●									●						●			
Dibenz(c,h)acridine	2.3E4	3.5E5	258	–	$C_{21}H_{13}N$		●									●						●			
Indeno(1,2-b)quinoline			217	410	$C_{16}H_{11}N$		●									●						●			
Indeno(1,2,3,i,j)isoquinoline			203		$C_{15}H_9N$		●									●						●			
C. Pyrrole and Fused Ring Derivatives of Pyrrole																									
Pyrrole	2.7E3	4.0E4	67	130	C_4H_5N		●								●							●			
Indole	1.1E4	1.7E5	117	254	C_8H_7N		●								●							●			
Methylindoles	4.5E4	6.8E5	131	270$^\pm$	C_9H_9N		●								●							●			
Carbazole	2.3E4	3.4E5	167	355	$C_{12}H_9N$		●									●					●	●			
Methylcarbazoles			181	195	$C_{13}H_{11}N$		●								●						●	●			
Benzo(a)carbozole	1.9E4	2.8E5	217	450	$C_{16}H_{11}N$		●									●					●	●			
Dibenzo(a,g)carbozole	6.0E3	9.0E4	267	–	$C_{20}H_{13}N$		●									●					●	●			
Dibenzo(a,i)carbozole	1.2E4	1.8E5	267	–	$C_{20}H_{13}N$		●									●					●	●			
Dibenzo(c,g)carbozole	1.0E3	1.5E3	267	–	$C_{20}H_{13}N$		●									●						●			
D. Nitrogen Heterocycles containing additional Heteroatoms																									
Benzothiazole	4.3E3	6.4E4	135	231	C_7H_5NS		●								●							●			
Methyl benzothiazoles	4.7E3	7.1E4	149	238	C_8H_7NS		●								●							●			

[1] Health effects basis (µg/m³) [2] Monoisotopic lightest isotope of each atom [3] TCO BP 100-300°C [4] GRAV BP > 300°C

8-22-78

Category 24

								Field GC																	
	MATE		MW[2]	BP	COMP	Air		SGC	GC Ramp						TCO[3]	GRAV[4]	LC Fraction								Comments
Heterocyclic Oxygen Compounds	Air[1]	Water		°C		Gas	SASS		1	2	3	4	5	6			1	2	3	4	5	6	7	8	
Furan			68	31	C_4H_4O	●							●												
Benzofurans			118	174	C_8H_6O		●								●						●				
Dibenzofuran			168	287	$C_{12}H_8O$		●								●						●				
Methyldibenzofurans			182	300±	$C_{13}H_{10}O$		●									●					●				
Naphthofurans			168	282	$C_{12}H_8O$		●								●						●				
Benzo[b]naptho[2,3-d]furan			218	395	$C_{16}H_{10}O$		●									●					●				
Phenanthro[9,10-b]furan			218		$C_{16}H_{10}O$		●									●					●				
1,9-benzoxanthene			218	400	$C_{16}H_{10}O$		●									●					●				

2-27-78

1 Health effects basis (µg/m³) 2 Monoisotopic, lightest isotope of each atom. 3 TCO BP 100-300°C 4 GRAV BP >300°C

Category 25

Field GC

	MATE		MW²	BP	COMP	Air		SGC	GC Range						TCO³	GRAV⁴	LC Fraction								Comments
Heterocyclic Sulfur **Compounds**	Air¹	Water		°C		Gas	SASS		1	2	3	4	5	6			1	2	3	4	5	6	7	8	
Thiophene	4.5E3	6.8E4	84	34	C_4H_4S	●							●												
Methylthiophenes	2.3E4	3.4E5	98	112 +	C_5H_6S		●								●					●					
Dimethylthiophenes			112	140 ±	C_6H_8S		●								●					●					
Trimethyl; and tetramethyl			126	170 ±;	$C_7H_{10}S$;		●								●					●					
thiophenes			140	170 ±	$C_8H_{12}S$		●								●					●					
2,2'-Bithiophene			166	260	$C_8H_6S_2$		●								●					●					
Benzo[b] thiophene	2.3E4	3.5E5	134	221	C_8H_6S		●								●					●					
Dibenzothiophene			152	332	$C_{12}H_8S$		●									●				●					
Benzonaphthathiphene	9.9E2	1.5E4	234	430	$C_{16}H_{10}S$		●									●				●					

1 Health effects base (ug/m³) 2 Monoisotopic, lightest isotope of each atom 3 TCO BP 100 - 300°C 4 GRAV BP > 300°C

2-24-78

Category 26

Organometallics

	MATE		MW[2]	BP	COMP	Air		SGC	GC Range						TCO[3]	GRAV[4]	LC Fraction								Comments
	Air[1]	Water		°C		Gas	SASS		1	2	3	4	5	6			1	2	3	4	5	6	7	8	
A. Alkyl or Aryl Organometallics																									
Trimethyl arsine			120	52	$As(CH_3)_3$	●							●												
Alkyl lead (TEL)	1.0E2	1.5E3	323	200	$Pb(C_2H_5)_4$		●								●		●								
Alkyl mercury (DMM)	1.0E1	1.5E2	226	96	$Hg(CH_3)_2$	●								●											
Organotin	1.0E2	1.5E3																							
Organogermanes	3.2E4	4.1E5																							
B. Sandwich Type Organometallics																									
Ferrocene	6.0E4	9.0E5	186	-	$Fe(C_5H_5)_2$		●									●	●								
Nickelocene	3.5E3	5.2E4	189	-	$Ni(C_5H_5)_2$		●									●	●								
Dibenzene chromium			206	-	$Cr(C_6H_6)_2$		●									●	●								
C. Metal Porphyrins and Other Chelates																									
Complexed Vanadium							●																		
Nickel							●																		
Copper	3.0E3	4.5E4					●																		
Iron							●																		
Tin							●																		
Zinc							●																		

Field GC

2-27-78

1 Health effects basis (µg/m³) 2 Monoisotopic, lightest isotope of each atom 3 TCO BP 100 300°C 4 GRAV BP >300°C

APPENDIX B

Partition Coefficients

The following table lists $\log_{10}$ partition coefficients for a wide range of species, tabulated according to MEG categories. The octanol data were taken from the work of Leo, et al.,[*] and the values for heptane and chloroform were calculated by the method described in that paper. The chloroform values are intended to approximate the values for methylene chloride, as it was not possible to calculate values for that solvent. The heptane values are given as appoximations of the pentane partition coefficients.

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[*] Leo, Albert, Corwin Hansch and David Elkins, "Partition Coefficients and their Uses," Chemical Review 71, 525 (1971).

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Appendix B*

Partition Coefficients for Sample MEG Compounds

No.	Category	Compound	LogP_{hept}	LogP_{CHCl_3}	LogP_{oct}
1	Aliphatic Hydrocarbons	--	large		-
2A	Saturated Alkyl Halides	1-Chlorobutane	-0.33	2.01	2.39
2B	Unsaturated Alkyl Halides	--	--	--	--
3	Ethers	Propyl Ether	1.53	2.76	2.03
4	Halogenated Ethers	--	similar to ethers		
5A	Primary Alcohols	1-Butanol	-1.88	0.37	0.92
		1-Pentanol	-1.28	1.0	1.49
5B	Secondary Alcohols	2-Butanol	-2.13	0.15	0.68
		2-Pentanol	-1.44	0.86	1.34
5C	Tertiary Alcohols	t-Butanol	-2.32	-0.07	0.5
		t-Pentanol	-1.40	0.89	1.37
6A	Glycols	Ethylene Glycol	-4.84	-2.67	-1.88
		Decamethylene Glycol	-1.51	0.78	1.27
6B	Epoxides	--	similar to ethers		
7A	Aldehydes	Acetaldehyde	-1.43	0.72	0.43
		Propionaldehyde	-1.52	0.66	0.38
		Butyraldehyde	-0.04	1.68	1.18
7B	Ketones	Acetone	--	0.38	--
		2-Butanone	-1.71	0.52	0.275
		2-Hexanone	0.33	1.93	1.38
8A	Carboxylic Acids	Acetic Acid	--	-1.55	--
		Valeric Acid	-1.37	0.30	1.4
		Hexanoic Acid	--	1.94	--
		Decanoic Acid	1.47	3.25	4.09
		Phenylvaleric Acid	-0.43	1.23	2.29
		Lauric Acid	1.58	3.30	4.20
		6-Phenylcaproic Acid	-0.32	1.36	2.40
8B	Carboxylic Acids with addnl. functional groups	Phthalic Acid	-2.56	-1.02	0.28
		Suberic Acid ($C_8H_{14}O_2$)	-2.11	-0.55	0.70
		Azelaic Acid ($C_8H_{26}O_2$)	-1.19	0.41	1.57
8C	Amides	Acetamide	--	-1.25	--
		Valeramide	-2.51	-0.26	0.32
		N,N-Diethylvaleramide	-0.88	1.44	1.87
9	Nitriles	Acetonitrile	-3.21	-1.0	-0.34
		Acrylonitrile	-2.75	-0.50	0.10
		Benzonitrile	-1.20	1.10	1.56
10A	Primary Amines	Ethylamine	-1.89	0.39	0.18
		Butylamine	-0.67	1.23	0.84
		Amylamine	-0.21	1.55	1.09
		Hexylamine	1.47	2.69	~2
		Aniline	--	1.30	--

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*See Section IIB-1 for application

No.	Category	Appendix B Compound	LogP_{hept}	LogP_{CHCl_3}	LogP_{oct}
10B	Secondary Amines	Diethylamine	-1.30	0.84	0.5
		Methylbutylamine	0.23	1.87	1.33
		Dipropylamine	0.97	2.38	1.73
10C	Tertiary Amines	Triethylamine	0.44	2.00	1.44
11	Azo Compounds, Hydrazine, and Derivatives	Hydrazine	0.05	1.35	1.23
12	Nitrosoamines	--	--	--	--
13A	Mercaptans (Thiols)	Butyl Mercaptan	1.99	3.07	2.28
13B	Sulfides, Disulfides	Methyl Disulfide	1.05	0.43	1.77
14A	Sulfonic Acids	Benzenesulfonic Acid	-5.24	-3.88	-2.26
		Paraiodobenzene-sulfonic Acid	-4.19	-2.76	-1.27
		Naphthalenesulfonic Acid	-4.57	-3.20	-1.63
14B	Sulfoxides	Dimethylsulfoxide	-4.99	-2.85	-2.03
(14C)	Sulfonic Acid Salts (Detergents)	Potassium dodecylbenzene Sulfonate	-2.32	-2.00	-0.36
		Sodium dodecylbenzene Sulfonate	-3.33	-1.11	-0.45
15	Benzene & Subst'd. benzene Hydrocarbons	Benzene	1.38	2.66	1.95
		Toluene	2.54	3.46	2.58
16A	Ring-subst. Halogenated Aromatics	Chlorobenzene	3.03	3.79	2.84
		1,2-Dichloro-benzene	4.02	4.47	3.38
		1,3-Dichloro-benzene	4.04	4.47	3.38
		1,4-Dichloro-benzene	4.04	4.49	3.39
16B	Aromatics w/Halogenated Alkyl Side Chains	α-Chlorotoluene	2.03	3.11	2.30
17	Aromatic Nitro Cmpds.	Nitrobenzene	1.21	2.54	1.86
18A	Monohydric Phenols	Phenol	-1.30	0.30	1.47
		Methylphenols (cresols)	-1.05	0.56	1.7
		Ethylphenols	-0.32	1.30	2.4
		Dimethylphenols	-0.42	1.30	2.3
18B	Dihydric & Polyhydric Phenols	1,2-Dihydroxy-benzene	-1.87	-0.30	0.93
		1,3-Dihydroxy-benzene	-2.13	-0.58	0.68
		1,4-Dihydroxy-benzene	-2.38	-0.85	0.45
		1,2,3-Trihydroxy-benzene	-2.58	-1.40	0.26
18C	Fused Ring Hydroxy Compounds	α-Napthol	0.30	2.00	2.98
		β-Napthol	-1.09	0.27	1.67
19	Halophenols	2-Chlorophenol	-0.42	1.30	2.3
		Chlorinated Cresols	0.40	2.11	3.08

Appendix B

No.	Category	Compound	$\text{LogP}_{\text{hept}}$	$\text{LogP}_{\text{CHCL}_3}$	LogP_{oct}
20	Nitrophenols	1,2-Nitrophenol	1.20	2.53	1.85
		1,3-Nitrophenol	-0.74	0.90	2.0
		1,4-Nitrophenol	-0.83	0.81	1.91
		Dinitrophenol	-1.05	0.58	1.71
		Trinitrophenol	-1.40	0.20	1.37
21	Fused Polycyclic Hydrocarbons	Naphthalene	3.84	4.36	3.28
22	Fused Non-Alternant Hydrocarbons	Indene	3.17	4.89	2.92
23A	Pyridine & Subst. Pyridines	Pyridine	-1.02	1.00	0.65
		Chloropyridine	0.20	1.84	1.31
23B	Fused 6-membered ring Heterocyclic N Cpds.	Quinoline	1.29	2.60	1.9
		Acridine	3.97	4.30	3.35
23C	Pyrrole & Fused Ring Derivs.	Pyrrole	-0.84	1.11	0.75
23D	Nitrogen Heterocycles Contg. Addnl. Heteroatoms	Benzothiazole	1.51	2.75	2.02
24	Heterocyclic Oxygen Compounds	Furan	2.71	3.58	2.67
25	Heterocyclic Sulfur Compounds	Thiophine	1.12	2.48	1.81
26	Organometallics	- -		no data found	

APPENDIX C

Specific Retention Volumes (V_g)* for Adsorbate Vapors on Sorbent Resins (20°C)

Adsorbate	Tenax-GC	XAD-2
n-Hexane	2.58×10^4	7.53×10^4
n-Octane	1.89×10^5	2.29×10^6
n-Decane	3.08×10^6	2.09×10^7
n-Dodecane	2.19×10^8	---
Benzene	6.09×10^4	5.24×10^4
Toluene	7.88×10^5	2.58×10^5
p-Xylene	3.81×10^5	9.05×10^5
Ethylbenzene	8.36×10^5	5.64×10^5
n-Propylbenzene	1.53×10^6	4.61×10^6
1,2-Dichloroethane	2.32×10^4	1.96×10^4
Fluorobenzene	8.82×10^4	3.13×10^4
1,1,2-trichloroethylene	8.82×10^4	3.06×10^4
Chlorobenzene	2.36×10^6	2.43×10^5
Bromobenzene	8.41×10^6	6.39×10^5
1,4-Dichlorobenzene	1.73×10^7	2.33×10^6
2-Butanone	2.21×10^4	4.39×10^3
2-Heptanone	5.55×10^6	1.49×10^6
4-Heptanone	3.22×10^6	1.52×10^6
Cyclohexanone	1.36×10^6	3.66×10^5
3-Methyl-2-butanone	6.46×10^4	2.53×10^4
3,3-Dimethyl-2-butanone	--	8.59×10^4
2,6-Dimethyl-4-heptanone	--	1.61×10^7
Acetophenone	1.23×10^7	7.70×10^6
n-Butylamine	2.67×10^4	1.80×10^4
n-Amylamine	1.96×10^5	1.29×10^5
n-Hexylamine	7.35×10^5	4.80×10^5
Benzylamine	1.58×10^6	7.87×10^6
Di-n-butylamine	1.91×10^6	6.90×10^6
Tri-n-butylamine	4.85×10^5	--

Specific Retention Volumes (V_g)* for Adsorbate Vapors on Sorbent Resins (20°C)

Adsorbate	Tenax-GC	XAD-2
Ethanol	9.08×10^2	1.75×10^3
n-Propanol	5.71×10^3	9.31×10^3
n-Butanol	4.34×10^4	2.07×10^4
2-Butanol	1.86×10^4	2.04×10^4
2-Methyl-2-propanol	7.08×10^2	1.60×10^3
2-Methyl-1-propanol	2.88×10^4	1.28×10^4
Phenol	2.47×10^6	3.68×10^6
o-Cresol	1.00×10^7	1.33×10^7
p-Cresol	1.40×10^7	1.51×10^7
m-Cresol	1.18×10^7	1.55×10^7
Acetic Acid	3.20×10^3	7.07×10^3
Propionic Acid	1.73×10^4	4.00×10^4
n-Butanoic Acid	1.04×10^5	7.74×10^4
n-Pentanoic Acid	5.53×10^5	2.89×10^5

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* In units of mL/g.